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SOIL SCIENCE

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CHEMICAL CHANGES DURING DECOMPOSITION OF PINEAPPLE TRASH UNDER FIELD CONDITIONS[1]

R. K. TAM AND O. C. MAGISTAD[2]

University of Hawaii

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In the Hawaiian pineapple fields approximately 100 tons (wet basis) per acre of unproductive old plants are commonly disked down or shredded and plowed under the surface soil after the second ratoon harvest. To a large extent the success of the following crop depends upon the nature and extent of decomposition of this incorporated trash.

Hawaiian pineapple soils have a very low carbon-nitrogen ratio of approximately 7.0 (3) as compared with a ratio of about 10 or more for soils from the mainland United States and other temperate regions. The addition and subsequent decomposition of pineapple trash profoundly alters this ratio. A carbon-nitrogen ratio slightly higher than 7.0 is desirable because of its stimulatory effect on soil microörganisms, which in turn directly influences plant growth. A carbon-nitrogen ratio above 12 to 1 is, on the other hand, undesirable because of the eventual conversion of available nitrogen to the unavailable form under conditions favoring rapid cell multiplication.

Throughout the literature of pedology one can easily locate extensive and comprehensive investigations on the decomposition processes of materials such as rye straw, peat, cottonseed meal, oak leaves, alfalfa, sweet clover, and other plants used for green manures. Starkey (12), in 1924, compiled a rather complete history of the study and progress of the decomposition of organic matter in soils. No effort toward a similar review will be attempted in this report.

Concerning the decomposition of the pineapple plant *Ananas comosus* (L.) Merr. in soil, a recent paper was published by Allen, Abel, and Magistad (1). This investigation was, however, primarily a microbiological approach to the subject and was carried out under artificial laboratory conditions supposedly optimum for the growth of microörganisms. Almost nothing is known of the chemical changes in pineapple trash under actual field conditions.

The primary purpose of the present investigation was to determine under field conditions the rapidity, order, and degree with which the constituents of shredded pineapple plants are changed during decomposition. To attain this

[1] Published with the approval of the director as Technical Paper No. 87 of the Pineapple Experiment Station, University of Hawaii.

[2] Scientific aide and chemist, respectively.

end, samples of soil and trash were obtained from an experimental area at regular intervals and studied chemically in the laboratory.

EXPERIMENTAL

An area of approximately one-half acre, located in one of the drier land areas on the island of Oahu, served as the experimental area in the present investigation. This area had been planted in the fall of 1930, and the following crops had been harvested: plant crop in 1932, first ratoon 1933, and second ratoon 1934. On November 1, 1934, a growth on this area of unproductive old pineapple plants approximating 100 tons per acre on the wet basis was shredded. The first weighings and samples for analysis were obtained on the same day, a few hours after shredding. Subsequent samplings were made at 2-week intervals; later samplings were made at 4-week or 6-week intervals as the cycle of decomposition progressed. Altogether 12 samplings were made in a period of 35 weeks.

Four weeks after shredding (November 30, 1934) this area was plowed and disk harrowed. Subsequent plowings were made on February 2, March 29, and May 2, 1935.

FIELD METHODS

The most useful and obvious criterion of decomposition in a field experiment is the reduction in total dry weight of the weighable organic matter incorporated into the soil. To obtain this index, field weights of measured subareas of trash were made. Weighable trash was arbitrarily taken as all organic material held on a 16-mesh sieve. Sample plots were 0.0003-acre squares. Weights were calculated to tons of trash per acre after corrections for moisture and adhering soil had been made on the basis of iron and aluminum determinations.

Mathematical analyses of previous trial weighings of trash showed that if 10 areas of 0.0003 acre were sampled at one time the resulting standard error would be small enough to give a reliable mean. Hence, all subsequent samplings were made on 10 sub-plots.

Weighings were made by piling the trash contained in the measured area into bamboo baskets. After the total weight was obtained the leaves were separated from the stumps[3] by hand. The stumps were then weighed separately, and the weight of the leaves was obtained by deducting the weight of the stumps from the total trash weight. Approximately one pound of leaves and one pound of stumps from each area were saved, appropriately combined, and taken to the laboratory for analysis. Leaves and stumps were analyzed separately as composites of ten 1-pound sub-samples. The remaining trash gathered from the sub-plots in the process of weighing was returned to the denuded areas after soil samples had been taken.

[3] The term "stump" is used locally to designate the stem of the pineapple plant. This is a massive central storage organ which in the mature plant ranges from 1 to 2 feet in length and 3 to 4 inches in diameter.

Soil samples were obtained through the use of soil augers. Two borings were made in each 0.0003-acre plot. The soil from each pair of plots (1+2, 3+4, etc.) was combined, making five topsoil samples (1 to 12 inches) and five subsoil samples (12 to 20 inches). Care was observed to mix thoroughly all soil samples prior to taking out a definite amount for laboratory analysis.

LABORATORY METHODS

Samples of leaves and stumps from the field were first thoroughly chopped up, then dried at 70°C., and this dried material was further subdivided by passage through a Wiley mill. All results are reported on the basis of material dried for 48 hours at 70°C.

Separate samples of both leaves and stumps were used in the analysis for moisture, total nitrogen, and total ash (2). Total iron plus aluminum was also determined (2). The results of the latter determination were employed in developing factors for the correction of adhering soil. Soil analyses showed that soil samples from the experimental area closely approximated 40 per cent iron plus aluminum oxides.

The methods used, with minor adaptations, in the present investigation for the determination of the different organic component parts were those employed by Waksman and Tenney (18) in their study of the composition and decomposition of natural organic materials. These methods were later modified and used by Waksman and Stevens (17) in their studies on the chemical composition of peat. Although the results reveal only the proximate composition and percentages of the various constituent parts, nevertheless they are convenient and useful indications of the chemical changes taking place in the course of decomposition of organic materials in the field.

It is unnecessary to repeat here the clearly presented methods of Waksman and Stevens (17). Because of differences in the nature of the organic material of the present investigation, attention should, however, be called to the following adaptations:

Ten-gram portions of pineapple leaf and stump material were used for analysis.

Soxhlet extracters were used in all three extractions: ether, hot water, and alcohol.

Through experimentation the following extraction periods resulted in comparatively complete extractions: ether 24–26 hours, hot water 16–18 hours, alcohol 4–6 hours.

Hydrolysis of hemicelluloses and celluloses was carried out in 500-cc. florence fiasks using a train of test tube condensers.

Reducing sugars were determined by the methods of Lane-Eynon (2) and Munson-Walker (2).

Total available nitrogen (ammonia plus nitrate) in soils was extracted by Harper's method (4) using 10 per cent NaCl and distilling with Devardo's alloy for nitrate reduction. This determination was made as soon after sampling as time permitted. Soil samples were then air-dried. Total nitrogen was determined on the air-dry soil by the method of Gunning and Hibbard (2); organic matter, by the wet oxidation method (5); available potassium,

by the method of Volk and Truog (16); and easily soluble phosphorus, by the method of Truog (15). Moisture determinations (2) were made and all results calculated on the dry soil basis.

DISCUSSION OF RESULTS

Dry weights

The dry weights of the pineapple trash at regular intervals throughout the decomposition period of 35 weeks are presented in table 1.

On November 1, 1934, at the time of shredding, the first weighings of trash were obtained. Means of ten 0.0003-acre areas showed the leaf fraction of the trash to be present at the rate of 18.6 tons per acre on the dry basis. The stumps had an average weight of 8.4 tons per acre, dry basis. This is a total trash weight of 27.0 tons per acre on the dry basis. Moisture determinations averaged 70 per cent for total trash. When a standard error of ±3.84 is

TABLE 1

Trash weights at various stages of decomposition in tons per acre—dry basis

(Corrected for adhering soil)

MATERIAL	WEEKS											
	0	2	5	7	9	11	13	15	19	23	29	35
Leaves	18.6	18.0	14.3	22.3	18.6	18.8	7.6	6.3	3.7	2.8	0.9	1.6
Stumps	8.4	8.2	6.1	5.5	5.2	7.5	4.0	4.0	1.7	1.8	1.6	1.6
Total trash	27.0	26.2	20.4	27.8	23.8	26.3	11.6	10.3	5.4	4.6	2.5	3.2

taken into consideration, it can be concluded that the average trash weight, on the wet basis, in this experimental area approximated 100 tons per acre. This is good average tonnage for other pineapple areas.

At the end of the 35-week decomposition period the following weights on the dry basis were obtained: leaf material, 1.6 tons; stump material, 1.6 tons; total trash, 3.2 tons, per acre. Calculations involving the weights obtained at the start of the experiment and those obtained at the end of 35 weeks show that 91 per cent of the leaf material and 81 per cent of the stump material had been decomposed.

Magistad (unpublished data) was able to obtain complete decomposition of finely chopped pineapple stems in 3 months in soils kept at 30 per cent moisture content under laboratory conditions. Under field conditions such a rapid rate of decomposition is impossible because of three important uncontrolled factors:

Incomplete mechanical disintegration of the pineapple plants during the process of shredding. Sometimes whole plants are merely uprooted and left on the surface to decompose.

Wide variation in the moisture supply, which is often so low as greatly to retard decomposition.

The available nitrogen supply varies widely between regions in which pineapple is grown.

At the end of the 35-week period it became evident that further decrease in weights would be extremely meager over an extended period. At this stage approximately 90 per cent of the total trash, both leaf and stump material, was made up of resistant hemicelluloses, celluloses, lignins, and crude protein. Such material, still in a slow process of decomposition, gradually approaches the final product commonly called soil "humus." With deep plowing this heterogeneous mass becomes an important agent in the physical improvement of pineapple areas low in organic matter.

From table 1 it is surprising to find that the trash weights obtained during the fourth, fifth, and sixth samplings were unusually high. It was discovered that this was due to an error in the sampling method. In the first six samplings, plots had been selected at various areas in the field most likely to give an average weight. This was not a truly random method of sampling, since personal judgment was a deciding factor. This method was revised, and from then on trash weights showed a consistent decrease as decomposition proceeded. In the revised method the field was laid out in a Latin square arrangement with provisions for 100 sampling plots. Selection of 10 plots for each of 10 samplings was then determined by the casting of dice.

ORGANIC FRACTIONS

Proximate chemical analyses of the various organic fractions in pineapple trash showed that the quantitative changes of the constituent fractions throughout the decomposition period of 35 weeks agreed fairly well with those reported by Tenney and Waksman (14) in their studies on mature corn stalks, rye straw, mature oak leaves, and mature alfalfa plants. Table 2 summarizes the total losses in per cent and in tons per acre of the various fractions for the decomposition period of 35 weeks.

Ether-soluble fraction. The ether-soluble fraction, comprising the fatty oils, nitrogenous fats, and parts of the wax-like and resin-like substances, showed a steady decrease throughout the period of decomposition. At the end of 35 weeks, 97.1 per cent of the original 0.69 tons per acre in the leaf material was no longer accounted for in the material held on a 16-mesh sieve. In the stump material 93.3 per cent had been decomposed.

Hot-water-soluble fraction. In both the leaf material and stump material this fraction along with the ether-soluble fraction showed the greatest per cent loss during the 35-week decomposition period. This loss in the water-soluble fraction is not surprising, since it has been shown time and again by numerous investigators that this fraction, containing the carbon compounds most easily available to microörganisms, always disappears readily and in the largest amounts.

Analyses for water-soluble reducing sugars showed an initial concentration in the leaf material of 5.94 per cent of the dry material. In 2 weeks this amount was reduced by over a half, 2.61 per cent remaining. In 5 weeks it had been reduced to a fraction of a per cent, and in 7 weeks only traces of re-

ducing sugars were detectable. This loss was almost identical in the case of stump material.

Water-soluble nitrogen showed a continuous drop from 0.26 to 0.11 per cent in the leaf material and from 0.32 to 0.14 per cent in the case of the stump material during the first 23 weeks. Thereafter an increase was detected, the leaf material showing a final percentage of 0.22 and the stump material a percentage of 0.24 at the end of 35 weeks. This increase in available nitrogen toward the end of the decomposition period can most probably be explained by the fact that most of the easily available carbon had been used up, thereby resulting in a reduction or limitation of the activities of the microörganisms carrying on the decomposition process. Death of the microörganisms was

TABLE 2

Losses in the various chemical fractions of pineapple trash due to a 35-week decomposition period

CHEMICAL CONSTITUENTS	LEAF MATERIAL						STUMP MATERIAL					
	Prior to decomposition, 18.6 tons/acre, dry		After 35 weeks, 1.6 tons/acre, dry		Loss		Prior to decomposition, 8.4 tons/acre, dry		After 35 weeks, 1.6 tons/acre, dry		Loss	
	Per cent composition	Tons/acre, dry basis	Per cent composition	Tons/acre, dry basis	Per cent loss	Tons/acre, loss	Per cent composition	Tons/acre, dry basis	Per cent composition	Tons/acre, dry basis	Per cent loss	Tons/acre, loss
Ether-soluble fraction	3.72	0.69	1.14	0.02	97.1	0.67	1.82	0.15	0.52	0.01	93.3	0.14
Hot-water-soluble fraction	27.13	5.05	8.75	0.14	97.2	4.91	23.14	1.94	8.03	0.13	93.3	1.81
Alcohol-soluble fraction	2.06	0.38	2.77	0.04	89.5	0.34	2.95	0.25	1.99	0.03	88.0	0.22
Hemicelluloses	19.08	3.55	22.54	0.36	89.9	3.19	29.54	2.48	20.11	0.32	87.1	2.16
Celluloses	24.92	4.64	38.30	0.61	86.9	4.03	16.88	1.42	35.48	0.57	59.9	0.85
Ash-free lignin	7.64	1.42	25.41	0.41	71.1	1.01	7.54	0.63	29.63	0.47	25.4	0.16
Crude protein	2.64	0.49	4.36	0.07	85.7	0.42	2.53	0.21	3.90	0.06	71.4	0.15
Total ash	5.90	1.10	9.09	0.15	86.4	0.95	3.19	0.27	7.22	0.12	55.6	0.15

accelerated, followed by disintegration of cell protein and subsequent release of available nitrogen. It is also true that the reduced carbon-nitrogen ratio at this stage encouraged an accumulation of nitrate. This was substantiated analytically by a corresponding reduction in crude proteins during the period of increasing available nitrogen. The foregoing results are in agreement with those of Martin (7) and Sturgis (13), who in decomposition studies have shown that nitrate accumulates along with the formation of soil humus.

Alcohol-soluble fraction. Although the percentage of this fraction at no time throughout the decomposition period showed a great variation, yet, when weights are considered, an evident loss can be shown to have occurred. No doubt the greater part of this loss was due to the destruction of the higher alcohols. The more resistant waxes, resins, tannins, and bitter substances

can be expected to make up the major portion of this fraction at the end of the 35-week period.

Hemicelluloses. Allen, Abel, and Magistad (1) found that under laboratory conditions hemicelluloses in chopped pineapple stumps and leaves showed a surprisingly low degree of decomposition although it was shown that a large percentage of the microflora of the soil was able to utilize this substance. Under field conditions it seems that a considerable loss occurs. The percentage of hemicellulose persisting in the trash at any given period throughout the cycle fluctuated consistently at approximately 20 per cent. This shows that the rate of decomposition of these compounds was in a fair proportion to the rate of decomposition of the total trash.

When the decomposition of hemicelluloses was computed on the basis of reduction in tons per acre, at the conclusion of the 35-week period, there was a loss of 89.5 per cent of the original 3.55 tons present in the leaf material. In the stump material a loss of 87.1 per cent was recorded. Tenney and Waksman (14) noted the following percentages of hemicelluloses remaining in various materials after a decomposition period: corn stalks, 12.35 per cent of the original after 405 days; rye straw, 53.22 per cent after 386 days; mature oak leaves, 54.91 per cent after 386 days; and alfalfa, 37.09 per cent after 405 days. Pineapple leaves and stumps compare favorably with corn stalks in that 10.1 and 12.9 per cent, respectively, remained after a somewhat shorter decomposition period of 245 days.

Cellulose. Cellulose is known to undergo decomposition to a fairly large extent under natural conditions, both aerobically and anaerobically. It is generally concluded, however, that the decomposition usually requires a greater length of time as compared to the rate of decomposition of the other plant constituents. This is especially true if it is combined with the most resistant of all plant substances, the lignins, to form ligno-celluloses.

In the present investigation 13.1 per cent of the original total cellulose in the leaf material remained after 35 weeks. In the stump material a far greater amount remained undecomposed, 40.1 per cent of the original 1.42 tons being detectable after 35 weeks. It is obvious that a far greater fraction of the cellulose in the stump material is in a more resistant form than that found in the leaf material.

Lignins. It has been generally concluded by the majority of investigators and has been proved that the most resistant fraction of natural organic materials is the lignins combined as ligno-proteins and ligno-celluloses. Pineapple trash conforms to this established contention.

Consistently rising percentages of lignin for both pineapple leaf and stump material definitely prove that the decomposition of this fraction did not keep pace with the decomposition of the other organic fractions or with trash taken as a whole. The original analysis showed an initial lignin concentration of 7.64 per cent in the leaf material and 7.54 per cent in the stump material. At the end of 35 weeks the concentration of lignin on the percentage basis had

increased to 25.41 per cent in the leaf material and 29.63 per cent in the stump material. Calculated on the dry weight basis per acre, however, the lignin showed a considerable reduction.

The decomposition of lignin was much faster in the leaf material than in the stump material. In the former case, after 35 weeks, only 28.9 per cent of the original amount remained, whereas in the case of the stump material 74.6 per cent was accounted for. From the residual lignin angle, pineapple leaf material compares favorably with corn stalks, and pineapple stump material is much akin to mature oak leaves (14).

The vast differences in the rate of decomposition of lignin between the two types of pineapple material can be explained by their differences in physical structure. The fibrous tissues, including nearly all of the lignins found in the pineapple leaf exist as thin strands which are easily attacked. In the stump material the fibrous tissues are much heavier in structure. The former physical type lends itself much more easily to mechanical disintegration, which in the present study is an accountable factor.

Crude protein. The percentage of crude protein rose steadily as decomposition proceeded, the sharpest rise occurring during the first 5 weeks. Toward the end of the 35-week period crude protein decreased slightly. Available nitrogen showed a reciprocal fluctuation, being reduced at the beginning and increasing toward the end of the decomposition period.

This rise and fall of both available nitrogen and crude protein can easily be explained from the microbiological standpoint, as previously referred to in the discussion of water-soluble nitrogen.

SOIL

In any field decomposition study of organic materials, soil analyses of the experimental areas are indispensable because of the intimate relation between material and soil. Table 3 summarizes the results of soil analyses performed in the present study. Among the most important determinations is the quantitative relationship of total carbon to total nitrogen. In any soil undisturbed for a long time, a definite equilibrium between carbon and nitrogen tends to be established. Cultivation, with the addition of carbonaceous or nitrogenous materials, changes this ratio. Reversion to the normal ratio is a constant process (11). Other important quantitative determinations are those of total available nitrogen, available potassium, and easily soluble phosphorus.

Carbon-nitrogen ratio. Dean (3) in a summary of 223 Hawaiian pineapple soils has shown that the average carbon-nitrogen ratio under local climatic conditions is very near 7 to 1. The organic matter content was analyzed by the method of Rather (8, 9), which probably gave too high results due to incomplete removal of the hydrated colloids of the soil.

Using the wet combustion method (5) to determine the organic matter in

TABLE 3

Quantitative chemical changes of various compounds in soil during a decomposition period of 35 weeks

CHEMICAL ANALYSES	WEEKS											
	0	2	5	7	9	11	13	15	19	23	29	35
Surface soil												
Organic matter.....*per cent*	1.90	1.96	1.88	1.92	1.95	1.85	1.96	1.98	1.82	1.84	2.02	2.06
Total carbon.....*per cent*	1.10	1.13	1.09	1.12	1.13	1.07	1.14	1.15	1.06	1.07	1.17	1.19
Total nitrogen.....*per cent*	0.23	0.21	0.20	0.22	0.21	0.21	0.21	0.21	0.21	0.21	0.23	0.23
Carbon-nitrogen ratio.....	4.8	5.4	5.5	5.2	5.4	5.1	5.4	5.5	5.0	5.1	5.1	5.2
Available nitrogen.....*p.p.m.*	40	23	30	34	30	29	40	25	24	20	27	36
Easily soluble phosphorus.....*p.p.m.*	5	.....	4	.....	3	.....	3	.....	.....	.....	7	6
Available potassium.....*m.e./100 gm.*	0.31	.....	0.35	.....	0.41	.....	0.49	.....	.....	.....	0.90	1.03
Subsoil												
Organic matter.....*per cent*	0.97	0.99	0.80	0.96	0.93	0.91	1.09	0.94	0.84	0.75	0.82	1.09
Total carbon.....*per cent*	0.57	0.57	0.47	0.56	0.54	0.53	0.63	0.55	0.48	0.43	0.48	0.64
Total nitrogen.....*per cent*	0.15	0.12	0.10	0.12	0.11	0.12	0.14	0.12	0.12	0.12	0.14	0.15
Carbon-nitrogen ratio.....	3.8	4.8	4.7	4.7	4.9	4.4	4.5	4.6	4.0	3.6	3.4	4.3
Available nitrogen.....*p.p.m.*	19	15	7	12	12	10	25	17	18	22	20	20

85 Hawaiian pineapple soils, Magistad (unpublished data) obtained a carbon-nitrogen ratio lower than 7 to 1. A summary of Magistad's results show:

FIELD NUMBER	PER CENT TOTAL ORGANIC MATTER	PER CENT TOTAL NITROGEN	C:N RATIO
1 Kunia	2.86	0.280	5.9
15 Kunia	2.55	0.267	5.5
19 Kunia	2.84	0.281	5.9
302 Molokai	1.58	0.187	4.9
321 Molokai	1.74	0.196	5.4

In the present investigation, a very low carbon-nitrogen ratio of 4.8 to 1 was obtained prior to the incorporation of the pineapple trash (table 3). With the shredding of 27 tons (dry basis) of trash, approximately 58 per cent of which is carbon, the carbon-nitrogen ratio was raised to 10.8 (fig. 1). Approximately 360 pounds of nitrogen was contained in the 27 tons of trash. This was taken into consideration in the carbon-nitrogen ratio calculations.

At the end of the 35-week decomposition period the carbon-nitrogen ratio resulting from the analysis of 16-mesh soil sampled to a depth of 1 foot was 5.2. The calculated carbon-nitrogen ratio, which takes into consideration the undecomposed residue of the incorporated trash, was 5.9; this ratio had dropped from 10.8 in the 35 weeks (fig. 1).

The difference between the analyzed ratio of 5.2 and the calculated ratio of 5.9 is attributed to the resistant fractions of trash which withstood decomposition in the 35-week period; namely, the ligno-celluloses, the ligno-proteins, and some hemicelluloses. This residue in a slow and relatively constant rate of chemical change will finally approach the chemical state of soil "humus." Resisting further decomposition, this heterogeneous mass becomes an important factor in the physical improvement of our pineapple soils low in organic matter.

Available nitrogen. Throughout the 35 weeks of decomposition, available nitrogen in the surface foot of soil never dropped below 20 p.p.m. (fig. 2). This was to be expected because of the very low carbon-nitrogen ratio and despite the fact that it was raised to 10.8 with the addition of trash. Russell (10) places the critical carbon-nitrogen ratio, below which nitrate accumulates, at 12 to 1.

Decrease in the available nitrogen of the topsoil with an increase in the subsoil during the thirteenth, fifteenth, nineteenth, and twenty-third weeks was the result of heavy spring rains. At one time (twenty-third week) the available nitrogen of the subsoil was actually greater than that of the topsoil. Available nitrogen in the topsoil showed a constant increase during the dry summer months.

Replaceable potassium. An interesting result of the soil analysis was the continual increase in replaceable potassium in the soil throughout the decom-

position period of 35 weeks (table 3). Replaceable potassium actually increased from 0.31 to 1.03 m.e. K_2O/100 gm. soil, or from 350 to 1160 pounds

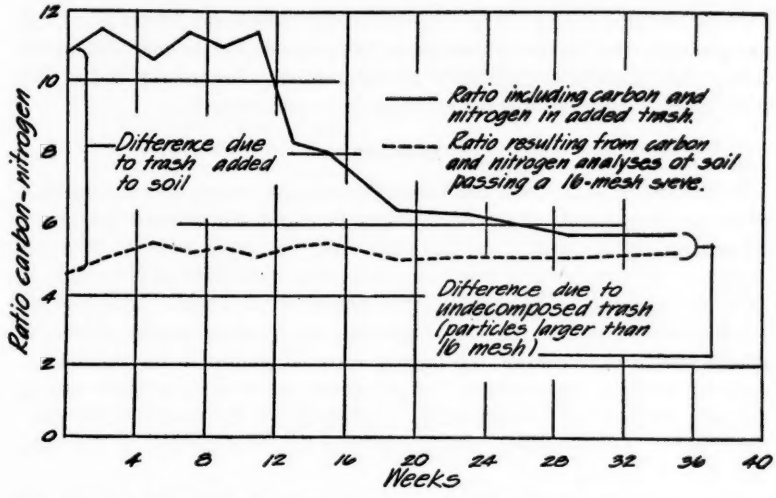
Ratio carbon-nitrogen
Weeks
Ratio including carbon and nitrogen in added trash.
Ratio resulting from carbon and nitrogen analyses of soil passing a 16-mesh sieve.
Difference due to trash added to soil
Difference due to undecomposed trash (particles larger than 16 mesh)

FIG. 1. SOIL CARBON-NITROGEN RATIOS DURING A 35-WEEK DECOMPOSITION PERIOD OF PINEAPPLE TRASH

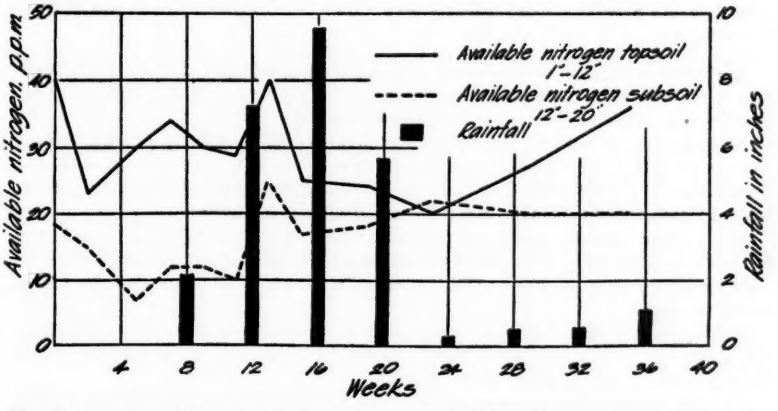

FIG. 2. AVAILABLE NITROGEN OF SOILS DURING A 35-WEEK DECOMPOSITION PERIOD OF PINEAPPLE TRASH
(P.p.m., dry basis)

per acre foot of soil on the basis of 2,400,000 pounds of soil per acre foot. This increase was undoubtedly due to the release of replaceable potassium from the decomposing material. According to Magistad (6) probably no

response by pineapple plants would result from potassium fertilization of a soil containing over 0.5 m.e. K_2O/100 gm. soil.

Easily soluble phosphorus. The presence of this element in the soil showed a steady decrease during the first 13 weeks of decomposition (table 3). This was probably due to the utilization of this element by the microörganisms during their most active period of decomposition. Toward the end of the cycle, easily soluble phosphorus returned to its original level.

SUMMARY

To determine under field conditions the rapidity, order, and degree with which the constituents of shredded pineapple plants are changed during decomposition, approximately one-half acre of old pineapple plants with a top growth of 100 tons per acre (wet basis) was tractor-shredded on November 1, 1934, and allowed to decompose for a period of 35 weeks. It should be pointed out clearly that this period includes the months generally highest in rainfall and that, therefore, the organic material studied in the present experiment received the benefit of a large amount of necessary moisture during the early stages of its decomposition. Application of the results of the present study to decomposition periods involving the drier months of the year may lead to serious errors.

At regular intervals during the decomposition period leaf, stump, and soil samples were chemically analyzed. The term "stump" is used locally to designate the stem of the pineapple plant—a massive central storage organ which in the mature plant ranges from 1 to 2 feet in length and 3 to 4 inches in diameter.

At the end of the 35-week decomposition period the residual leaf material was only 9 per cent of the original 18.6 tons per acre dry leaf portion of the trash. Of the original 8.4 tons of stumps (dry basis), 19 per cent remained undecomposed.

All of the organic fractions found in trash underwent decomposition to a certain degree, some proceeding at a greater rate than others. In the order of increasing resistance to decomposition, the various fractions were as follows: water-soluble fraction, ether-soluble fraction, alcohol-soluble fraction, hemicelluloses, celluloses, and lignins.

Water-soluble reducing sugars were decreased from 5.94 per cent to 2.61 per cent in the leaf material during the first 2 weeks of decomposition. At the end of 7 weeks only traces of reducing sugars were detectable. This loss was also shown to be true in the case of the stump material.

Crude protein in trash increased as decomposition proceeded, whereas water-soluble nitrogen decreased. During the last 12 weeks a decrease in crude protein was detected with a corresponding increase in water-soluble nitrogen.

The original soil carbon-nitrogen ratio was 4.8 to 1. With the addition of 27 tons of trash (dry basis), approximately 58 per cent of which was carbon, the ratio was increased to 10.8. At the end of 35 weeks of decomposition the carbon-nitrogen ratio was reduced to 5.9, 3.2 tons of residual trash held on a 16-mesh sieve being taken into consideration. The carbon-nitrogen ratio of 16-mesh soil was 5.2.

Recent carbon-nitrogen ratio studies including the present investigation tend to show that the ratio in certain Hawaiian soils is even narrower than the 7 to 1 ratio reported by Dean (3) in 1930. A ratio of 5 or 6 to 1 seems to be a closer approximation for the drier land areas reported in this paper.

Available nitrogen in soils decreased during the first 23 weeks of decomposition but increased during the last 12 weeks.

Replaceable potassium in soil continually increased from 0.31 to 1.03 m.e. K_2O/100 gm. soil, or from 350 to 1160 pounds per acre foot, during the 35-week period. This was released from the incorporated trash during decomposition.

Easily soluble phosphorus decreased during the earlier stages of decomposition, regaining its former level in the soil toward the end of the decomposition period.

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ZINC CONTENT OF SOILS IN RELATION TO PECAN ROSETTE

A. O. ALBEN AND HUGH M. BOGGS

Bureau of Plant Industry, U. S. Department of Agriculture

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In recent years zinc has been found to be an essential element for normal plant growth. It is not required in large amounts, however, and some plants or trees either require less of the element or are better able than others to obtain their needs from the same soil environment. The pecan is rather sensitive to a deficiency of zinc due either to insufficient amounts present in the soil or to its unavailability; this deficiency results in a condition of the tree known as "pecan rosette."

Several investigators (1, 2, 3, 4, 5) have controlled pecan rosette by using zinc salts, usually the sulfate, in one of three ways; namely, as a spray applied to the foliage, as an injection into the trunk, or as an application to the soil. The spray application is equally effective on any soil type. With the limited data available it would seem that trunk injections, when sufficient amounts are applied, are also equally effective on any soil type. On the other hand, soil applications in certain amounts are effective on some soil types, whereas on others the same or larger amounts have no effect.

Pecan rosette has not been observed on some soil types, whereas on other soil types rosette, unless controlled, is a limiting factor in pecan development. In Louisiana and Texas, pecan rosette is more prevalent on basic soils than on acid soils. All of the zinc present in soils may or may not be available to the trees. The availability of the zinc may depend on the chemical composition of the soil and possibly on its reaction. It is reasonable to expect that the amount present in the various soils might have something to do with supplying the tree's need for the element. This paper deals with the zinc content of several soils, soil reaction, and the prevalence of rosette.

Details of the method developed for determining the zinc content of the soils are to appear in another article. In brief, it consists of fusing the soil with potassium pyrosulfate and disintegrating the fusion in hot hydrochloric acid. The silica is removed by filtration, and the washings are evaporated. The acidity of the solution is fixed at 0.4 *N*, and the interfering members of the first hydrogen sulfide group are removed. The solution is buffered, a filter aid added, and the pH fixed at about 3.5. The zinc is precipitated with hydrogen sulfide, filtered, and dissolved with 1 *N* hydrochloric acid. The zinc in the acid solution is determined nephelometrically by the ferrocyanide method.

The total zinc content and the reaction of 32 soil profiles have been determined. All of these data are not presented here as they are not needed to bring out the points involved. The zinc content of the soil and the reaction were determined for depths varying from 3 to 12 feet, with most determinations made to a depth of 6 feet. On cultivated soils the soil samples were taken at intervals of 0–6, 6–12, 12–24, 24–36 inches, etc.

The total zinc content varies considerably in the soils used in the determinations. The highest amount found in an acre 6 inches was 146 pounds, and the smallest amount, 8 pounds. These figures for the zinc content and the ones used in the tables are computed on the basis of a weight of two million pounds for an acre 6 inches of soil.

The zinc content and the soil reaction of six calcareous pecan soils from Texas are given in table 1. The smallest amount of zinc in these basic soils

TABLE 1

Pounds of zinc per acre and reaction of six calcareous soils

DEPTH	CATALPA SILTY CLAY LOAM, BROWNWOOD, TEX.		FRIO SILTY CLAY LOAM, UVALDE, TEX.		CATALPA SILTY CLAY LOAM, CIRCLEVILLE, TEX.		CATALPA CLAY LOAM, GEORGETOWN, TEX.		CATALPA SILTY CLAY LOAM, LOW PHASE SECOND BOTTOM, LULING, TEX.		CATALPA SILTY CLAY LOAM, THIRD BOTTOM, LULING, TEX.	
	Zinc	pH	Zinc	pH	Zinc	pH	Zinc	pH	Zinc	pH	Zinc	pH
inches	*lbs.*		*lbs.*		*lbs.*		*lbs.*		*lbs.*		*lbs.*	
0–6	126	8.10	106	7.70	76	7.40	146	8.00	106	7.55	86	8.40
6–12	126	8.20	106	7.70	66	7.40	146	7.70	106	7.40	86	8.40
12–24	212	8.25	212	7.23	232	7.55	252	7.77	252	7.15	152	8.40
24–36	292	8.35	252	7.20	212	7.40	252	7.70	252	7.52	172	8.30
36–48	212	8.40	252	7.80	...	....	...	....	...	....	...	....
48–60	232	8.55	252	7.75	...	....	...	....	...	....	...	....
60–72	232	8.50	252	8.10	...	....	...	....	...	....	...	....
Total to 36...	756	....	676	....	586	....	796	....	716	....	496	....

for any one 6-inch soil horizon is 66 pounds, and the largest amount is 146 pounds. The total amount of zinc in an acre from the surface down to 36 inches varies from 496 to 796 pounds. The soil reaction is above pH 7 for all the horizons sampled. Pecan trees have rosetted severely in all the locations where the soil samples were taken except one which is of special interest: when these soil samples were taken pecan trees were not rosetting in the second bottom on the Luling, Texas, farm. All the pecan trees planted on the third bottom were rosetting severely. Table 1 shows that the amount of zinc is considerably lower and the soil reaction is higher in the third bottom than in the second.

The zinc content per acre 6 inches and the soil reaction for six soils with both acid and basic horizons are given in table 2. The smallest amount of zinc is 8 pounds, and the largest is 126 pounds for an acre 6 inches of soil.

The total zinc content for an acre to a depth of 36 inches varies from 112 to 756 pounds. The soil reaction for the horizons varies from pH 5.75 to pH 9.08. The rosette condition of pecan trees varies considerably in the orchards from which the soil samples given in table 2 were taken. The writers have never observed any rosette in the orchard from which the Monroe silt loam sample

TABLE 2

Pounds of zinc per acre and reaction of soils with both acid and basic horizons

DEPTH	MONROE SILT LOAM, MONROE, LA.		ACADIA VERY FINE SANDY LOAM, HOUSTON, TEX.		WINDTHORST FINE SANDY-LOAM, CALCAREOUS PHASE, STEPHENVILLE, TEX.		WINDTHORST SANDY LOAM, RISING STAR, TEXAS		PLEDGER SILTY CLAY LOAM, BRAZORRA, TEXAS		YAHOLLA LOAM, SHREVEPORT, LA.	
	Zinc	pH	Zinc	pH	Zinc	pH	Zinc	pH	Zinc	pH	Zinc	pH
inches	*lbs.*		*lbs.*		*lbs.*		*lbs.*		*lbs.*		*lbs.*	
0–6	86	6.10	8	6.45	18	7.70	18	7.05	126	7.00	50	7.50
6–12	86	5.75	18	6.30	22	7.75	22	7.00	126	6.92	50	7.46
12–24	172	5.75	68	6.60	84	6.80	36	6.00	252	7.64	92	7.35
24–36	192	7.47	84	7.00	116	6.50	36	5.90	252	7.87	60	7.00
36–48	172	8.35	76	7.25	52	8.10	...	....	252	7.85	60	6.85
48–60	132	9.07	116	7.67	...	....	...	....	212	8.00	100	6.55
60–72	172	9.08	124	8.00	...	....	...	....	212	8.15	52	6.50
Total to 36...	536	....	178	....	240	....	112	....	756	....	252	....

TABLE 3

Pounds of zinc per acre and reaction of some acid soils

DEPTH	OCKLOCKONEE FINE SANDY LOAM, TOLEDO, TEX.		RUSTON FINE SANDY LOAM, CADDO PARISH, LA.		NORFOLK FINE SANDY LOAM, CADDO PARISH, LA.		NORFOLK FINE SANDY LOAM, WINONA, TEXAS	
	Zinc	pH	Zinc	pH	Zinc	pH	Zinc	pH
inches	*lbs.*		*lbs.*		*lbs.*		*lbs.*	
0–6	66	6.00	26	6.15	18	6.10	18	5.58
6–12	66	5.10	24	5.95	18	5.60	14	5.60
12–24	132	5.15	68	5.45	36	5.20	52	5.00
24–36	132	4.88	84	5.52	44	5.40	52	5.00
36–48	132	4.35	100	5.25	...	....	52	5.10
48–60	132	4.25	100	5.20	...	....	52	5.60
60–72	...	....	...	....	...	....	52	5.20
Total to 36...	396	....	202	....	116	....	136	....

was taken. This soil has a relatively high zinc content and an acid reaction of the soil to a depth of 24 inches at least. The orchards on all the other soils given in the table have rosette in varying degree of severity, but none of them have rosette as severely as the orchards from which the soil samples given in table I were taken. Rosette is not particularly severe in the orchard which has the lowest zinc content. The soil reaction is only slightly alkaline in the

surface horizon, neutral in the 6–12 inch horizon, and basic in the 12–36 inch horizon.

The zinc content per acre 6 inches and the soil reaction for four acid soils are given in table 3. The zinc content varies from 14 to 66 pounds per acre 6 inches and from 116 to 396 pounds for an acre to a depth of 36 inches. The soil reaction for the horizons varies from pH 4.25 to pH 6.15. No rosette has been observed in the pecan orchard on the Ochlockonee fine sandy loam from which the soil sample was taken. The zinc content of 396 pounds for an acre 0–36 inch horizon is almost half of the amount present in most of the basic soils shown in table 1. The Ruston fine sandy loam soil has a zinc content of 202 pounds per acre for the 0–36 inch horizon. The whole profile tested is decidedly acid. Pecan trees are not rosetting in this part of the orchard. The zinc content in this profile is less than a third of that of most of the soil profiles shown in table 1. The two Norfolk soils have a very low zinc content. The soil reaction is acid for both profiles. In the parts of the orchards from which these samples were taken pecan trees are rosetting.

The results given in this paper show that the zinc content of the basic soils examined is generally higher than the zinc content of the acid soils and that even though the basic soils contain appreciable quantities of zinc there is considerable rosette in pecan trees growing on these soils, indicating that the zinc is unavailable. On soils having both acid and basic horizons the trees, as indicated by rosette condition, seem to be favorably influenced by the acid horizons. Soils having all acid horizons support pecan trees relatively free of rosette when the soil contains a moderate quantity of zinc, indicating that this zinc is available. Acid soils containing very small quantities of zinc produce trees which rosette, indicating that the very small quantities of zinc which they contain, though available, are not sufficient for normal functioning of pecan trees. In studying the functions of zinc in the control of pecan rosette, it is indicated that the zinc content of the soil, as well as the chemical composition and the reaction of the soil, must be taken into consideration.

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THE RESPONSE OF RHIZOBIA TO NATURAL HUMIC ACID

FRANKLIN E. ALLISON AND SAM R. HOOVER[1]

Bureau of Chemistry and Soils, U. S. Department of Agriculture

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The results of studies (1, 2, 8) at this laboratory, confirmed recently by other investigators (11, 12), have shown that certain strains of legume nodule bacteria are unable to make an appreciable growth in an ordinary synthetic medium, prepared from pure chemicals, but require an additional substance previously designated as "coenzyme R." This material, which is essential for respiration and growth, is found widely distributed in plant and animal materials.

Other investigations (6, 7, 9, 10) with *Azotobacter chroococcum* and *Azotobacter vinelandii*, also carried out at this laboratory, have shown that the growth of these organisms is commonly increased from two- to five-fold by the addition of natural humic acid extracted from soil. This stimulation is due in large part to the iron which is present in such form that it is not readily precipitated.

These two lines of research suggest, therefore, that the growth stimulation produced by natural humic acid on rhizobia may be due not only to its content of the essential growth factor, but, in addition, to its available iron. The work reported in this paper was undertaken with the aim of learning more about the latter phase of the problem.

METHODS

The cultural medium, the same as that used previously (1), consisted of inorganic salts (without added iron), 1 per cent sucrose or dextrose, and 5 mgm. N (KNO_3, $NaNO_3$, or NH_4NO_3) per culture of 25 cc. The data reported in tables 1–4 were obtained by growing the organisms at 28°C. in 250-cc. Erlenmeyer flasks and making counts at intervals by means of a haemacytometer modified for bacterial counts. The results shown in figure 1 were obtained by the usual Warburg respiration technique. In this case the organisms were first grown in Erlenmeyer flasks, centrifuged under aseptic conditions, and 800 millions in 4 cc. of medium added to each sterilized Warburg vessel.

Natural humic acid was prepared (5) from a rich garden soil by extraction with alkali. Repeated precipitation with acid and dissolving in alkali mark-

[1] The writers are indebted to Drs. Dean Burk and C. A. Ludwig for numerous criticisms and helpful suggestions and to Mr. C. K. Horner for the preparation of some of the samples of humic acid used in these experiments.

edly reduces the coenzyme R content of the preparation. In the preparation of synthetic humic acid, described in detail elsewhere (10), sugar is boiled in strong H_2SO_4, the mixture centrifuged, and the solid phase extracted with

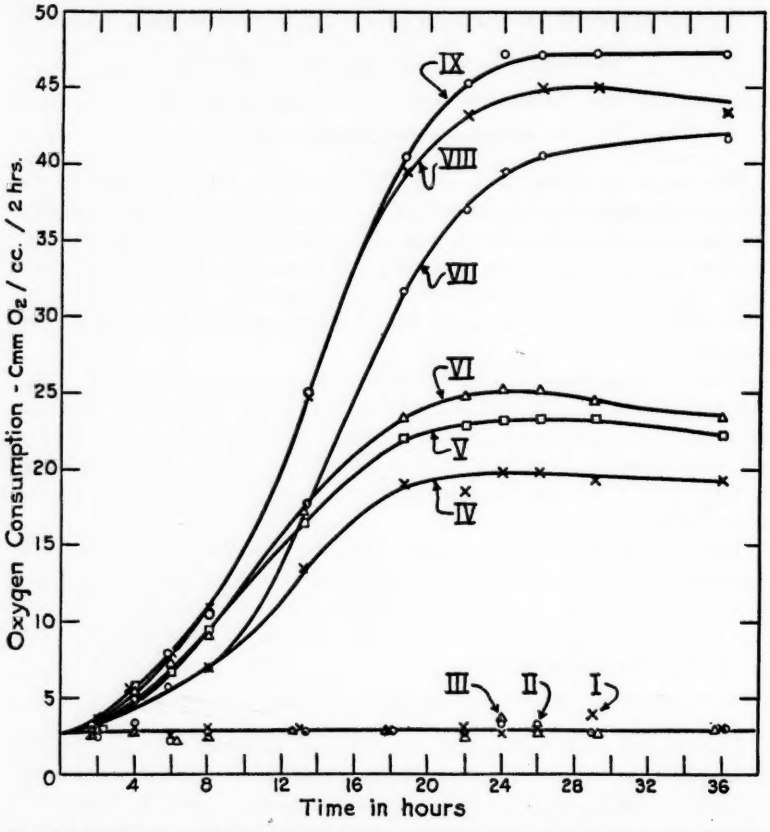

FIG. 1. THE EFFECT OF NATURAL AND SYNTHETIC HUMIC ACIDS AND OF COENZYME R UPON THE RESPIRATION OF RH. MELILOTI

I. Control. II. Synthetic humic acid (Fe = <0.01 per cent) 20 p.p.m. III. Synthetic humic acid (Fe = 10 per cent) 20 p.p.m. IV. Natural humic acid, 500 p.p.m. V. Coenzyme R, 2.4 p.p.m. VI. Coenzyme R, 2.4 p.p.m. + synthetic humic acid (Fe = 10 per cent) 20 p.p.m. VII. Natural humic acid, 1200 p.p.m. VIII. Coenzyme R 10 p.p.m. + synthetic humic acid (Fe = <0.01 per cent) 20 p.p.m. IX. Coenzyme R 10 p.p.m. + synthetic humic acid (Fe = 10 per cent) 20 p.p.m.

dilute alkali. C.P. ferric sulfate is added to supply the iron. The accessory factor for rhizobia was extracted from commercial sucrose with absolute alcohol. More concentrated preparations have since (8) been obtained from cultures of *A. vinelandii*, which synthesizes this factor.

The usual test organisms used were *Rhizobium trifolii*, strain 205, and *Rhizobium meliloti*, strain 131, obtained from I. L. Baldwin of the University of Wisconsin. The culture of *A. vinelandii* was obtained from J. G. Lipman, N. J. Experiment Station; *A. chroococcum* came from N. R. Smith of the Bureau of Plant Industry.

In these studies no attempt was made to eliminate the traces of iron from the basal medium. Only the effect of humic acid, when added to the usual type of synthetic medium, was determined. Even the better grades of dextrose and sucrose ordinarily (9) contain about 0.000009 to 0.0004 per cent iron as impurities, and this is not easily removed.

PHYSIOLOGICAL STUDIES

Experiment 1. The data, given in table 1, are typical of many results obtained showing the growth response of *Rhizobium* and *Azotobacter* to natural

TABLE 1

The effect of natural humic acid upon the numbers of Rh. trifolii *and* A. vinelandii *in a medium containing purified sugars*

HUMIC ACID (Fe = 0.45 PER CENT), P.P.M. DRY MATTER	MILLIONS OF BACTERIA PER CUBIC CENTIMETER			
	*Rh. trifolii**		*A. vinelandii*†	
	2 days	4 days	2 days	4 days
0	4	4	34	74
1			52	96
5	10	30	70	120
10			86	174
25	50		98	212
50			138	260
100	190		140	212
200	400	1200		
600	560	1760		

* Medium: inorganic salts, 1 per cent dextrose, and sodium nitrate.

† Medium: inorganic salts, 1 per cent sucrose, and no combined nitrogen.

humic acid. The marked difference between the magnitude of the response with the two types of organisms, and also the quantity of humic acid required to give a half maximum effect, are very striking.

No appreciable growth of the clover organism occurred in the absence of humic acid, but increasing additions up to the maximum used (600 p.p.m.) caused increased numbers almost in direct proportion to the quantity added. At the higher rates of application, even within the short incubation period of 2 to 4 days, the growth was extremely heavy—1760 millions per cubic centimeter in one case in contrast to 4 millions in the control.

The growth response with *A. vinelandii* was of a very different type. A fairly good growth occurred in the control and a four-fold increase above this where an optimum quantity of humic acid was added. A half-maximum

growth was obtained with 5 p.p.m., whereas 50 p.p.m. gave approximately a maximum effect. The same concentration of humic acid produced only a relatively small effect upon rhizobia when contrasted with the effect of the maximum application of 600 p.p.m. These data are in agreement with the results previously published (1) showing that *Rh. trifolii* requires a growth-producing substance which is present in natural humic acid. They also show that, although *Azotobacter* does not require the factor, it does manifest a marked growth response to humic acid, which, as recently shown (5, 6, 7, 9), is due in large part to its available iron content.

TABLE 2

The effect of humic acid and other sources of iron upon the growth of Rh. trifolii *in a medium* containing commercial sucrose*

TREATMENT	QUANTITY ADDED, P.P.M. DRY MATTER	MILLIONS OF BACTERIA PER CUBIC CENTIMETER			
		2 days	3 days	5 days	8 days
Check	0	60	200	400	840
Natural humic acid (Fe = 0.45 per cent)	10	156	320	780	1000
Natural humic acid (Fe = 0.45 per cent)	100	320	620	940	1380
Natural humic acid (Fe = 0.45 per cent)	1000	500	840	2000	2500
Synthetic humic acid (Fe = 3.5 per cent)	10	98	300	620	1040
Synthetic humic acid (Fe = 3.5 per cent)	100	126	400	580	1000
Synthetic humic acid (Fe = 3.5 per cent)	1000	126	420	610	620
Synthetic humic acid (Fe = trace)	10	74	202	500	620
Synthetic humic acid (Fe = trace)	100	110	320	610	680
Synthetic humic acid (Fe = trace)	1000	106	320	620	640
Ferric citrate	1	62	210	620	1040
Ferric citrate	10	94	320	610	840
Ferric citrate	50	82	300	580	860
Ferric sulfate	1	58	300	620	1020
Ferric sulfate	10	68	300	620	800
Ferric sulfate	50	90	320	620	820

* Medium: inorganic salts, 1 per cent commercial sucrose, and potassium nitrate.

Experiment 2. Table 2 shows a typical set of data obtained when various iron sources were tested on *Rh. trifolii* using a commercial sucrose which contained a considerable amount of coenzyme R.

The growth in the control under these conditions was good, in contrast to practically no growth in the control in the preceding experiment. Additions of natural humic acid up to the maximum used, 1000 p.p.m., again produced very heavy growths. Synthetic humic acid, which contained only a small amount of coenzyme R but a very high percentage of available iron, gave a two-fold increase in growth over the check in a few cases, but usually less than this. The synthetic humic acid, containing only a trace of iron, gave still smaller growth increases. Likewise, ferric citrate and ferric sulfate gave slight growth increases but in no case were the effects comparable to those produced by natural humic acid.

Experiment 3. The results of a direct comparison of the response of two species of *Rhizobium* and two of *Azotobacter* to synthetic humic acid (Fe = 10 per cent) and to a preparation of coenzyme R, used singly and in combination with humic acid, are given in table 3. The synthetic humic acid, used alone, gave no increase in growth of *Rh. trifolii* and only a comparatively small effect with *Rh. meliloti.* The increased growth of *Azotobacter* was almost as large as that produced by natural humic acid (table 1). Coenzyme R, used singly, produced a good growth of the two species of *Rhizobium*, but the concentration used was insufficient for a maximum effect. *A. chroococcum* gave no response to the material, and *A. vinelandii*, only a slight increase. From other experiments, not reported here, it is evident that this slight stimulation was due to

TABLE 3

The growth of Rhizobium and Azotobacter in the presence of synthetic humic acid and coenzyme R

TREATMENT, P.P.M. DRY MATTER	MILLIONS OF BACTERIA PER CUBIC CENTIMETER						
	First experiment*			Second experiment†			
	Rh. trifolii	*Rh. meliloti*	*A. chroococcum*	*Rh. trifolii*	*Rh. meliloti*	*A. vinelandii*	
	5 days	5 days	5 days	4 days	4 days	2 days	4 days
Check	40	30	40	50	30	30	80
Humic acid 5				44	40	80	180
Humic acid 10	40	40	100				
Coenzyme R 10	120	200	40				
Coenzyme R 20				320	310	32	110
Humic acid 5† Co. R 20				400	400	62	160
Humic acid 10† Co. R 10	180	200	100				
Ferric Sulfate (Fe ≏ Fe in humic acid)				40	36		

* Basal Medium: inorganic salts, 1 per cent c.p. sucrose, and ammonium nitrate.

† Basal Medium: inorganic salts, 1 per cent c.p. sucrose (nearly Fe-free), and potassium nitrate.

a trace of iron present in the preparation. Where both the humic acid and growth substance were added the growth of the two strains of *Rhizobium* was on the average about 25 per cent greater than with coenzyme R alone present. This effect was presumably due chiefly to the available iron supplied by the synthetic humic acid. The growth of *Azotobacter* was approximately the same whether humic acid was used alone or together with coenzyme R. Ferric sulfate, where added to *Rhizobium* cultures containing no added accessory factor, produced no growth response.

Experiment 4. In an attempt to determine more accurately the importance of available iron for rhizobia the experiment reported in table 4 was carried out. A sample of natural humic acid and also one of a synthetic humic acid, prepared both with and without the addition of inorganic iron (9), were

tested separately and in the presence of varying amounts of the coenzyme preparation. The iron content of all flasks containing humic acid was 1 p.p.m., which is adequate to give a maximum effect with *Azotobacter*. The coenzyme preparation was not especially concentrated, hence the relatively high concentrations used.

Natural humic acid produced the usual marked increase in growth (10- to 20-fold), when compared with the control containing basal medium only. However, where the coenzyme preparation was present, the additional effect of the natural humic acid was relatively small (25–35 per cent increase). The sample of natural humic acid to which 9.5 per cent additional iron was added produced only a slight increase in growth; in fact, a growth response corresponding approximately to the natural humic acid added and not to the iron content.

TABLE 4

The effect of natural and synthetic humic acids upon the growth of Rh. trifolii *in media containing varying concentrations of coenzyme R*

HUMIC ACIDS ADDED, P.P.M. DRY MATTER	MILLIONS OF BACTERIA PER CUBIC CENTIMETER ON 3rd DAY Additions of Coenzyme R, p.p.m. dry matter			
	0	40	80	160
Check	42	300	500	700
Natural humic acid 200	460	560	680	860
Natural humic acid (with added iron) 10	66	320	500	780
Synthetic humic acid, low Fe, 100	24	280	480	720
Synthetic humic acid, high Fe, 10	22	300	500	600

Note: The iron content of all flasks containing humic acid was the same—1 p.p.m. The basal medium contained inorganic salts, 2 per cent c.p. sucrose, and potassium nitrate.

The data of table 4 furnish little evidence that *Rh. trifolii* needs highly available iron in appreciable amounts. The basal medium used, made from c.p. sucrose and c.p. salts and with no added iron, contained practically all of this element needed. The data do show very conclusively, however, that *Rh. trifolii* requires a growth factor. If the experiment had been continued for a longer time so as to obtain heavier growths the need for iron might have been more in evidence.

Experiment 5. The Warburg respiration technique, using a heavy suspension of the organisms, was used in a number of experiments. Figure 1 gives a typical set of results. The data are reported in terms of the volume of oxygen consumed per cubic centimeter of culture per 2-hour period. The increase in oxygen consumption with time, over this 36-hour interval, is a measure of growth.

In the basal medium, containing none of the necessary growth substance (curve I), the respiration remained essentially constant at the very low value corresponding to that of the heavy inoculum over the period of the experiment.

The addition to this medium of synthetic humic acid, whether free from iron (curve II) or whether containing iron (curve III), had no appreciable effect on growth or respiration in the absence of coenzyme R. In contrast, the addition of natural humic acid at the rate of 500 p.p.m. (curve IV) produced a marked increase in respiration which reached a maximum in about 20 hours. Likewise, the coenzyme preparation, used alone (curve V), caused a rapid increase in oxygen consumption. The curve in this case was similar to that of natural humic acid (curve IV) except that the concentration used happened to give a somewhat higher oxygen utilization. Where both the coenzyme preparation and high-iron synthetic humic acid were used together (curve VI) the total oxygen consumption was greater than with the concentrated growth substance alone. Although this additional growth, presumably due largely to the iron in the synthetic humic acid, was definitely positive, the increase was less than 10 per cent. At higher concentrations (curves VII, VIII, IX) the iron effect was approximately the same as at the lower concentrations (curves IV, V, VI).

Figure 1 shows, therefore, that it is the bacterial growth substance in natural humic acid which is responsible for most (at least 90 per cent) of the increased growth of *Rh. meliloti*, following its addition to the medium. The remaining effect is due to the other constitutents present, chiefly available iron.

In previous publications the authors have pointed out that one of the unusual characteristics of coenzyme R is that its addition to a culture frequently causes a two- to four-fold increase in the rate of respiration during the first few hours before an increase in numbers occurs. In similar experiments natural humic acid gave a two- to three-fold effect and at the concentrations used was only slightly lower than the corresponding figures for the coenzyme preparation. This is further evidence that the important constituent in the two materials for rhizobia is the same.

It should be pointed out that a number of investigators (4) have shown that either molybdenum or vanadium is essential for nitrogen fixation by *Azotobacter*. Horner and Burk (9) and Burk (3) likewise observed that a portion of the effect of various iron sources on *Azotobacter* may, in some instances, be due to traces of molybdenum or vanadium present as impurities. Experiments in which we added these elements directly to the medium showed no growth response by rhizobia. The effect of other elements present as impurities in the iron sources used was not investigated.

SUMMARY

Experiments with two species of legume nodule bacteria, *Rh. trifolii* and *Rh. meliloti*, are reported, showing that the addition of natural humic acid to a synthetic (sugar-inorganic salts-nitrate) medium produces a marked increase in bacterial numbers and oxygen consumption. The growth obtained, over the concentration range of 0–600 p.p.m. dry matter, was nearly propor-

tional to the quantity added. In the absence of humic acid, and where a very pure sugar was used, no appreciable growth occurred.

Synthetic humic acids, prepared by boiling sugar in sulfuric acid, failed to produce a corresponding growth response on rhizobia. This held true regardless of the iron content of such preparations.

The growth response of the clover and alfalfa nodule bacteria to natural humic acid is due almost wholly to the presence of an essential growth substance, and not to the available iron content. This substance, coenzyme R, is essential for respiration and growth of these organisms.

The iron requirements of rhizobia are small. The stimulating effect of additions of available iron was usually less than 10 per cent in a synthetic medium prepared from C.P. ingredients.

A. chroococcum and *A. vinelandii*, used in comparative studies, showed no growth response to coenzyme R.

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NUTRITION OF BLUEBERRY (VACCINIUM CORYMBOSUM L.) IN SAND CULTURES[1]

CHARLES A. DOEHLERT AND JOHN W. SHIVE

New Jersey Agricultural Experiment Station

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The purpose of this investigation was the determination of some of the fundamental nutritional requirements of the blueberry plant (*Vaccinium corymbosum* L.) by laboratory and greenhouse experimentation. Such facts, it is felt, may be applied to conditions in the field to assist in arriving at an improved fertilizer practice for cultivated blueberries.

The fertilization of New Jersey blueberry soils has received attention since 1920 when Beckwith (1) reported favorably on a complete fertilizer. Revisions of this mixture have been recommended by Beckwith and Coville (3) and by Beckwith and Doehlert (4). The fundamentals of commercial blueberry culture were first determined by Coville (8), who reported in 1910 on extensive experiments showing this plant's peculiar need for an acid, peaty soil abundantly supplied with moisture but also well aerated. The application of these principles was pioneered by New Jersey growers who still produce almost the entire output in this new industry. The soil used is a native peat plowed and mixed with the sand subsoil. The locations selected for this purpose are practically all on St. John's sand or on swamp as classified by Lee, *et al.* (13). The reaction of these soils is reported as pH 3.5 to pH 4.5 by Beckwith (2) in a description of cranberry soils.

METHODS

The sand culture studies with blueberries were started May 12, 1932, in the plant physiology greenhouses. The main series of 20 cultures was carried through three growing seasons including two fruit harvests, with the loss of one culture (number 10) due to spray injury. Blueberry cuttings (*Vaccinium corymbosum* L.) of the Rubel variety, which had been rooted one year previous in Holland peat, were used. The peat was carefully washed from the roots, and the cuttings were planted in pairs in 3-gallon percolator urns filled with washed quartz sand. The plants were watered daily with tap water for one week before any nutrient treatments were applied.

The technique of applying nutrients to these cultures is that described and used by Spencer and Shive (20) in their studies of the nutrition of another

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ericaceous plant, *Rhododendron ponticum* L. The same four salt solutions were used except that in the present study they were made up to an osmotic concentration of one-half atmosphere instead of one atmosphere as used by Spencer and Shive. The components of these solutions are shown in table 1. The solution numbers listed in column two of this table designate 20 representative solutions selected from the Tottingham (23) series of 84. These numbers refer to the position which the solutions and cultures occupy in the four-coördinate scheme employed by Tottingham to represent the series in diagram. This table also shows the partial volume-molecular concentrations

TABLE 1

*Partial volume-molecular concentrations of KH_2PO_4, $Ca(NO_3)_2$, $MgSO_4$, and $(NH_4)_2SO_4$ in the solutions used**

CULTURE NO.	SOLUTION NO.	GRAM MOLECULES PER LITER OF SOLUTION			
		KH_2PO_4	$Ca(NO_3)_2$	$MgSO_4$	$(NH_4)_2SO_4$
1	$T_1\ R_1\ C_1$	.00105	.00073	.00829	.0007
2	C_3	.00105	.00219	.00592	.0007
3	C_5	.00105	.00365	.00355	.0007
4	C_7	.00105	.00511	.00118	.0007
5	$R_3\ C_1$	.00105	.00073	.00592	.0021
6	C_3	.00105	.00219	.00355	.0021
7	C_5	.00105	.00365	.00118	.0021
8	$R_5\ C_1$	.00105	.00073	.00355	.0035
9	C_3	.00105	.00219	.00118	.0035
10	$R_7\ C_1$	.00105	.00073	.00118	.0049
11	$T_3\ R_1\ C_1$	.00316	.00073	.00592	.0007
12	C_3	.00316	.00219	.00355	.0007
13	C_5	.00316	.00365	.00118	.0007
14	$R_3\ C_1$	.00316	.00073	.00355	.0021
15	C_3	.00316	.00219	.00118	.0021
16	$R_5\ C_1$	.00316	.00073	.00118	.0035
17	$T_5\ R_1\ C_1$	.00527	.00073	.00355	.0007
18	C_3	.00527	.00219	.00118	.0007
19	$R_3\ C_1$	.00527	.00073	.00118	.0021
20	$T_7\ R_1\ C_1$	.00738	.00073	.00118	.0007

* Osmotic concentration of each solution 0.5 atmosphere.

(gram-molecules per liter of solution) of the salts as they were used. In tables 2–4 the solutions are described by the brief method of referring to the proportional contribution of each salt to the total osmotic concentration.

Following the plan for rhododendron, the modification of Tottingham's series by Jones and Shive (12) was used in these experiments also. This requires the substitution of ammonium sulfate for potassium nitrate in equivalent partial osmotic concentration.

The solutions were applied to the surface of the sand by the continuous drip method set up as by Shive and Stahl (19). The rate of flow averaged 1,100

cc. a day. Iron was supplied in the form of ferrous sulfate in the proportion of 0.5 p.p.m. Tap water was used once a week for flushing in order to avoid undue accumulation of salts due to loss of water by transpiration and by evaporation from the surface of the sand and also to prevent undue changes of pH due to differential ion absorption. After the first seven weeks boron was supplied in the form of boric acid, and manganese, as manganese sulfate, both elements in the proportion of 0.5 p.p.m.

Four pairs of additional cultures were supplied with solution $T_1R_1C_5$ at each of four different concentrations; viz., 0.25, 0.50, 0.75, and 1.00 atmosphere. After two seasons the cultures at the highest concentration had made somewhat less growth than those at the other three concentrations, but other differences were not markedly significant.

For two winter periods, September 26, 1932, to March 19, 1933, and September 2, 1933, to April 19, 1934, the plants were wintered in outdoor shelters just outside the greenhouses. For the growing season of 1933 the cultures were returned to the greenhouse and treated as before. There had been a light set of fruit buds. When the blooms opened they were hand pollinated at 2- or 3-day intervals from April 6 to 19, inclusive. A small crop of fruit was harvested in 1933. The data for this crop are not tabulated here since the larger yields of 1934 present more significant differences.

During the growing season of 1934, the plants were kept in an outdoor shelter, screened with tobacco cloth, at the cranberry and blueberry substation. Advantages prompting this move were additional facilities for daily care and observation and for cross pollination by bees. Some of the plants were 4 feet tall at this time with an equal spread laterally for the combined tops of the paired plants. But there was no evidence of any pot-bound condition either at this time or when the roots were removed from the urns at the end of the experiment. At this time the constant drip method of renewing the solutions was discontinued and the solutions were poured upon the surface of the sand in the morning and the late afternoon. Each culture was supplied with the same solution as before. Because of weather changes, the quantity varied from 1 to 2 liters a day, and during wet weather, applications were occasionally omitted. More than two consecutive applications were never omitted, however. When rainfall was not frequent the cultures were flushed with tap water.

It has already been noted that boron and manganese were not applied during the first seven weeks of experimental treatment. This lapse of time was required to reveal deficiency symptoms, which were characterized by the browning and killing of the tips of a few rapidly growing shoots and the appearance of irregularly shaped red-brown areas on some leaves. Within a few days after application of boron and manganese, growth was again normal, and no recurrence of these symptoms took place in the series of cultures 1–20.

Two available extra cultures not included in the main series or in the series of eight cultures used to test the four concentrations were used as checks, from

which boron and manganese were again withheld. The symptoms noted before reappeared. Addition of the two elements again resulted in normal growth. Once more in this same growing season this process was repeated. After wintering out of doors, these cultures were returned to the greenhouse and allowed to fruit. One continued to receive boron and manganese, while the other was again deprived of these elements. The former culture matured normal fruit, but the berries on the latter wilted slightly when half ripe and then slowly shriveled. Seed development in these shriveled berries was poor and meager. No cultures were set up which separated the effects of the two elements.

Deficiency symptoms in other plants caused by the lack of boron have been described by Warington (24), Brenchly and Warington (5), Johnston and Dore (10), McHargue and Calfee (16), and McMurtrey (17). Deficiency symptoms caused by the lack of manganese have been described by McHargue (14, 15). There is at present, in the literature, no reference to such deficiency studies with the blueberry.

From the findings of these workers, it would be reasonable to assume that the brown discoloration of leaves and the destruction of the growing tips of the blueberry were due to an insufficient supply of boron, whereas the failure of one culture to ripen fruit and mature seeds was, perhaps, evidence of the unsatisfied need for manganese. No symptom such as these have been noted in the blueberry plantations.

RESULTS

Many of the experimental plants made excellent growth and yielded good crops of fruit. None were stunted in growth, and all produced some fruit. Field plants bearing 370 grams of ripe berries to the bush in the third season after propagation, and accompanied by good vegetative growth, would be considered thrifty plants (cf. table 2).

The harvest of fruit from the experimental plants in 1934 was accomplished in ten pickings of ripe berries, distributed over a period of two months. These yields were recorded for individual plants as fresh weights, since facilities for drying so many lots of material were not available at the substation. As the ripe fruit was removed from each bush it was immediately weighed and recorded.

The average yields per culture are arranged in order of descending magnitude in table 2, which also shows, adjacent to each average yield, the osmotic proportions of the salts in the nutrient solution used. The five high-yielding cultures grouped at the top of the table are characterized, with respect to treatment, by low mono-potassium phosphate. With the exception of culture 1, they are also characterized by high nitrogen.

The dry weights of the tops, exclusive of fruit, are similarly arranged in order of descending magnitude in table 3. The five highest of these are also

characterized by high nitrogen and, except for culture 18, by low monopotassium phosphate.

The blueberry naturally overbears. This results in a sharp reduction of leaf area, shoot growth, and food reserves in the current season and, further, in a smaller crop in the following season. Fruit production is the ultimate purpose of the grower. But the simultaneous production of foliage and new wood so largely determines the next crop that the two indexes of growth are

TABLE 2

Actual fresh weights and relative weight values of berries harvested

CULTURE NO.	WEIGHT OF FRUIT HARVESTED			RELATIVE WEIGHT VALUES*	RELATIVE OSMOTIC PROPORTIONS OF THE SALTS IN THE SOLUTIONS USED			
	Plant I	Plant II	Average		KH_2PO_4	$Ca(NO_3)_2$	$MgSO_4$	$(NH_4)_2SO_4$
	gm.	*gm.*	*gm.*					
9	...	461	461	147	1	3	1	5
7	473	324	398	127	1	5	1	3
3	243	484	363	116	1	5	3	1
4	328	364	346	110	1	7	1	1
1	303	326	314	100	1	1	7	1
5	282	308	295	94	1	1	5	3
2	338	202	270	86	1	3	5	1
11	104	408	256	82	3	1	5	1
15	224	...	224	71	3	3	1	3
8	125	204	165	52	1	1	3	5
18	158	...	158	50	5	3	1	1
19	114	178	146	46	5	1	1	3
13	119	150	134	43	3	5	1	1
16	201	53	127	40	3	1	1	5
12	...	120	120	38	3	3	3	1
6	125	51	88	28	1	3	3	3
14	59	108	83	26	3	1	3	3
17	82	30	56	18	5	1	3	1
20	44	...	44	14	7	1	1	1

* Computed on the basis of culture 1 as 100.

practically of equal importance in the evaluation of nutritional effect. Therefore, to obtain a truer picture of plant performance in response to nutrition, the relative production values for fruit and tops have been combined and averaged. It is not very likely that the equal weighting of these two values expresses exactly the ratio of their importance, but in the absence of quantitative data the method is adopted as the one most consistent with our experience with this plant. Relative values for yield of fruit and tops combined are given in table 4. It is particularly significant that here the best five cultures.

without exception, are those receiving treatments low in mono-potassium phosphate and high in nitrogen. Conversely, the solutions applied to the poorest yielding group of five cultures are characterized by high phosphate and low nitrogen. The high-yielding group is also characterized by treatments in which high proportions of calcium nitrate and, generally, low proportions of ammonium sulfate predominate.

TABLE 3

Actual dry weights and relative dry weight values of plant tops

CULTURE NO.	DRY WEIGHT OF TOPS			RELATIVE WEIGHT VALUES*	RELATIVE OSMOTIC PROPORTIONS OF THE SALTS IN THE SOLUTIONS USED			
	Plant I	Plant II	Average		KH_2PO_4	$Ca(NO_3)_2$	$MgSO_4$	$(NH_4)_2SO_4$
	gm.	*gm.*	*gm.*					
3	227	309	268	191	1	5	3	1
18	252	...	252	180	5	3	1	1
7	302	194	248	177	1	5	1	3
6	283	203	243	174	1	3	3	3
2	231	227	229	164	1	3	5	1
4	184	263	224	160	1	7	1	1
9	...	222	222	158	1	3	1	5
13	177	213	195	139	3	5	1	1
11	137	203	170	122	3	1	5	1
15	168	...	168	120	3	3	1	3
8	131	184	158	113	1	1	3	5
5	140	156	148	106	1	1	5	3
20	143	...	143	102	7	1	1	1
16	201	81	141	101	3	1	1	5
1	149	131	140	100	1	1	7	1
19	122	106	114	82	5	1	1	3
14	58	170	114	81	3	1	3	3
12	...	108	108	77	3	3	3	1
17	105	75	90	65	5	1	3	1

* Computed on the basis of culture 1 as 100.

DISCUSSION

There is an unusually close relation between the results obtained with these sand culture studies and the results of field work carried out by Beckwith and Doehlert (4). Field experiments conducted by these workers showed the greatest return of fruit with the use of nitrate of soda alone, but they conclude that the benefit of a complete fertilizer may have been obscured by excessive applications of rock phosphate. This is in agreement with the present sand culture experiments, which have shown maximum production by cultures receiving solutions low in mono-potassium phosphate and high in nitrogen. Further sand culture studies with greater replication are desirable.

Because of this agreement with field experiments and also because of the sandy nature of blueberry soils, it was felt that the methods of these experiments might be applicable to fertilizer investigations using ordinary blueberry soil. During the third season, therefore, a few plants potted in soil were treated regularly with solution $T_1R_1C_7$ (table 1). The growth obtained was so encouraging that it seems very likely that studies of this sort with typical blueberry soil and commercial fertilizer salts could assist in solving the problem of economical and effective fertilization of blueberry plantings. Such studies

TABLE 4

Comparison of relative production values for tops and fruit combined

CULTURE NO.	RELATIVE WEIGHT VALUES			RELATIVE OSMOTIC PROPORTIONS OF THE SALTS IN THE SOLUTIONS USED			
	Tops	Fruit	Average	KH_2PO_4	$Ca(NO_3)_2$	$MgSO_4$	$(NH_4)_2SO_4$
3	191	116	153	1	5	3	1
7	177	127	152	1	5	1	3
9	158	147	152	1	3	1	5
4	160	110	135	1	7	1	1
2	164	86	125	1	3	5	1
18	180	50	115	5	3	1	1
11	122	82	102	3	1	5	1
6	174	28	101	1	3	3	3
1	100	100	100	1	1	7	1
5	106	94	100	1	1	5	3
15	120	71	95	3	3	1	3
13	139	43	91	3	5	1	1
8	113	52	82	1	1	3	5
16	101	40	70	3	1	1	5
19	82	46	64	5	1	1	3
20	102	14	58	7	1	1	1
12	77	38	57	3	3	3	1
14	81	26	53	3	1	3	3
17	65	18	41	5	1	3	1

are now under way at the New Jersey Cranberry and Blueberry Substation. The continuance of the substation's field experiment which now includes a treatment very low in rock phosphate should be a helpful parallel.

In the middle group of nine cultures shown in table 4, there are four which received solutions low in phosphate. Of these four, two (cultures 1 and 5) received solutions low in nitrogen and high in magnesium sulfate, while the other two (cultures 6 and 8) received solutions fairly high in both nitrogen and magnesium sulfate. The evidence can be taken as a suggestion that the plant's need for magnesium is slight and that its growth processes may be easily retarded by an excess over this need.

The superiority of nitrate nitrogen over ammonium nitrogen is not surprising, inasmuch as the reaction of the nutrient solutions is about pH 4.5. The leachings are often as acid as pH 3.4. Various investigators, such as Tiedjens and Robbins (22), Tiedjens and Blake (21), Clark and Shive (7), and Davidson and Shive (9), have shown for several plants that anion nitrogen is absorbed more readily from a medium at relatively low pH than from a medium at relatively high pH, whereas cation nitrogen is absorbed more readily from a medium at high pH than from one at low pH.

The effect of potassium is not separated from that of phosphate. Shive (18) has conducted extensive investigations with soybeans using monobasic phosphates. In many cases injury occurred which he attributed not to the cations (Na, NH_4, K, Ca, and Mg) but to the common group H_2PO_4, or to the ions resulting from the partial dissociation of this group.

The blueberry is apparently more sensitive to variations in proportions of mono-potassium phosphate than is the rhododendron. Spencer (unpublished data) reports for rhododendron that "No injurious effects of solutions high in mono-potassium phosphate were evident. On many of the plants receiving high phosphate solutions the leaves presented a slightly wavy appearance along the margins instead of spreading out perfectly smooth and flat as in the case of the other leaves. This condition of the leaves, however, could hardly be regarded as detrimental to the plant since it was scarcely noticeable in most instances except only after very close inspection."

Other investigators at widely separated points working on different soils with blueberries in field plots have reported on the effect of phosphatic fertilizer. Johnston (11) in Michigan field tests with *Vaccinium corymbosum* did not find evidence of a low phosphorous requirement for blueberries. In his investigations, applications of superphosphate as heavy as 670 pounds to the acre resulted in profitable increases of yield, as compared with treatments with half as much superphosphate. On the other hand, Chandler and Mason (6) state that, in Maine, wild blueberries (*Vaccinium pennsylvanicum*) responded very favorably to fertilizers furnishing nitrogen, whereas "the plants on the plots receiving only phosphorous and potash were not much better than those on the untreated plots."

SUMMARY

Sand culture experiments with four-salt solutions were used to determine the nutritional needs of the cultivated blueberry (*Vaccinium corymbosum* L.).

Good vegetative growth and fruit production, as compared with field standards, were obtained.

The best nutrient solutions for the blueberry were low in phosphate and high in nitrogen.

Nitrate nitrogen under the conditions of these experiments was of greater value than ammonium nitrogen for this particular species.

There is agreement between the results obtained by the sand-culture,

nutrient-solution method of growing plants and the results obtained with blueberries in the field.

The need for boron and manganese was shown. Deficiency symptoms appeared during relatively short periods when these elements were withheld and were promptly eliminated when they were supplied.

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THE ESTABLISHMENT OF MOISTURE EQUILIBRIUM IN SOIL

FORREST SHREVE AND WILLIAM V. TURNAGE

Desert Laboratory, Carnegie Institution of Washington, Tucson, Arizona

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For a period of 5 years, fortnightly determinations of moisture content have been made at the Desert Laboratory in an alluvial clay soil at eight depths to 6 feet, with biennial determinations to 12 feet. The results for the first 40 months have been published by the senior author.[1] The soil in question has been found to exhibit rather slow changes with reference to both increase and decrease of moisture content. At a depth of 6 feet the moisture content varies less than 2 per cent during periods of 1 to 2 years.

In connection with this work the question arose as to the length of time that would be required for two immediately contiguous bodies of soil with different initial amounts of water to come to equilibrium, resulting in uniform moisture content throughout the two bodies. The ideal conditions for the answering of this question would require that both bodies of soil be protected from any addition of water by rainfall and any loss by evaporation and also that they be protected from changes of temperature and barometric pressure. A simple experiment was devised in which the addition and loss of water were prevented but in which temperature and pressure were not controlled.

The plan of the experiment was to make up several lots of soil to known percentages of water content, to place two or three layers of widely different content in large cans, and to sample the cans at intervals to discover the extent to which the establishment of equilibrium was taking place.

The soil used was one which closely resembles a large percentage of the agricultural soils of Arizona—an alluvial clay, or adobe, from the flood plain of the Santa Cruz River, near Tucson. The mechanical composition of the soil is described in the paper just cited, its most important feature being that from 78 to 89 per cent will pass a 0.05-mm. sieve. The maximum water holding capacity of the lot of soil used in the experiment was 33.2 per cent, but other samples of the same type of soil run as high as 49 per cent. A quantity of the soil was air dried. (It then had 1.1 to 1.4 per cent of moisture as determined from oven-dried samples, or an average of 1.3 per cent.) Each sample was made up to known moisture content by thorough mixing, placed in the can a little at a time, and thoroughly tamped into place with a heavy iron 8 inches in diameter. The top of each layer was level, smooth, and firm before any

[1] Shreve, Forrest 1934 Rainfall, runoff and soil moisture under desert conditions. Ann. Assoc. Amer. Geogr. 24: 131–156.

material for the next layer was placed on it. Stout garbage cans 60 cm. in depth by 35 cm. in diameter were used. Two cans were filled with two layers only and two others cans with three layers. The soil was brought to within 8 cm. of the top of the can and covered with a disk of galvanized iron resting on the soil. The disk was sealed to the wall of the can with plastilene, which was easily removed and replaced whenever the cans were opened for moisture determinations. The customary type of lid with deep flange was placed on each can. The cans were left outdoors in the complete shade of a small building throughout the experiment. The extreme annual range of air temperature to which they were subjected was, however, about 85°F. The sampling of the cans was done with a borer of 20 mm. diameter specially constructed for the purpose. In the cans with two layers, three samples were taken in each layer, and in those with three layers, two samples in each layer. The samples were 5 cm. in length and were so taken as to avoid the immediate vicinity of the line of junction between layers. The hole made by sampling was filled with soil closely approximating the moisture content of the soil removed, which could be estimated by color, and was thoroughly tamped into place. Each boring was made vertically from a different spot on the soil surface.

Since the initial water content of each can was known, it was possible to determine the error of sampling in each boring by averaging the six determinations made in each can. Most of the averages are close to the known moisture content, but some of them are high. It is evident that the error of sampling was not constant. A discrepancy of 1.3 per cent is to be expected because the layers were originally made up from air-dry soil whereas the moisture of the borings was determined from oven-dried material. It is probable that there was some horizontal movement of moisture, which might have been aided by the temperature changes to which the cans were subjected, and that some of the samples were not representative of the horizon from which they were taken. The duration of the experiment suggested the possibility that considerable moisture might have been lost from the surface layer by leakage and by evaporation at the time the cans were opened for sampling. After the close of the experiment two of the cans were opened and their entire moisture content determined by bringing the soil to air-dry condition. Can 4 was one of the two with driest surface layer. The borings taken in it at the end of the second year indicated an average moisture of 5.5 per cent, as compared with the initial 5 per cent. The actual moisture content for all of the soil in this can was 4.7 per cent (air-dry), indicating a small loss. Can 1 had the wettest surface layer. The borings in it at the end of the second year indicated an average of 15.2 per cent moisture, as compared with the initial 15 per cent. The entire body of soil was also removed from this can and found to have only 12.8 per cent moisture, indicating a much greater loss than in can 4. The failure of the final borings to indicate the actual loss by evaporation is probably due to the fact that no samples were taken in the uppermost 4 cm. of any cans at any of the readings.

In table 1 are shown the arrangement of the layers, their initial moisture contents, and the contents as determined on alternate months for the first year and at the end of the second year.

In can 1 there were two layers, the upper with 20 per cent, the lower with 10 per cent moisture. At the end of the first 2 months this can had gone half way

TABLE 1

Percentages of initial and subsequent moisture content, on dry weight basis, for layers of soils, together with arrangement of layers and times of sampling

CAN NUMBER	NOVEMBER, 1931	JANUARY, 1932	MARCH, 1932	MAY, 1932	JULY, 1932	SEPTEMBER, 1932	NOVEMBER, 1932	NOVEMBER, 1933
1	20	17.6	16.1	15.5	16.0	17.0	19.2	16.3
		17.6	15.7	16.1	16.4	16.5	19.5	16.1
		17.4	17.0	16.0	16.6	17.2	19.5	16.5
	10	15.5	14.9	15.3	14.9	14.3	20.7	13.9
		16.0	14.9	14.1	14.3	14.8	16.7	14.4
		15.3	15.7	14.3	15.8	14.7	14.1	14.3
2	5	4.6	6.7	6.7	7.3	7.4	5.7	8.1
		5.3	7.9	8.3	9.6	8.7	7.1	8.6
		7.3	10.6	9.5	11.2	8.9	7.7	9.5
	15	13.0	13.8	13.5	13.8	13.6	12.2	13.1
		13.2	13.5	....	13.7	13.3	12.1	12.7
		13.2	13.5	13.2	13.4	....	....	....
3	15	13.1	13.5	13.0	13.1	13.1	11.2	12.2
		13.3	13.2	13.1	13.3	13.3	12.6	13.0
	10	11.3	12.6	11.3	11.9	11.7	10.1	12.2
		10.7	11.6	11.0	11.2	11.2	10.2	12.2
	5	7.6	8.9	9.3	9.4	9.8	7.6	11.8
		6.7	7.7	8.1	8.9	10.3	8.8	12.3
4	5	8.3	6.9	4.4	5.4	5.0	3.9	3.7
		6.2	5.1	4.7	5.1	4.5	4.2	3.7
	0	3.8	4.0	4.0	5.0	4.9	4.4	3.8
		4.5	5.3	5.3	6.7	6.9	5.1	4.5
	10	9.1	8.7	8.0	8.8	9.1	7.8	8.4
		10.7	9.3	7.4	8.6	9.1	7.9	8.7

toward the establishment of equilibrium; during the first year it showed little tendency to progress further toward equilibrium. Also there is little indication of the effect of gravity on the movement of moisture or of a localized change of moisture in either layer near the line of contact. The readings taken

in this can in November 1932 are evidently too high, whereas those taken in November 1933 are close to the known average and are very similar to those taken in July 1932. In short, during the 22 months between the first and last readings on can 1 it had made no greater progress toward the establishment of equilibrium than it did in the first 2 months.

In can 2 there were two layers, the upper with 5 per cent and the lower with 15 per cent moisture. At the end of the first period this can had not gone so far toward equilibrium as can 1, doubtless because the layer with higher initial moisture was below, instead of above, the drier one. All readings in can 2 show a higher moisture content in the bottom of the upper layer, where it was contiguous to the layer with 10 per cent greater moisture, but they fail to show a progressive tendency for the moisture from the 15 per cent layer to move toward the top of the 5 per cent layer. In a soil of such fine texture this behavior is probably due in only a slight degree to the influence of gravity, and is more probably the result of the absence of evaporation from the surface of the 5 per cent layer. There is evidence in the later readings that the upper layer became more uniform in its content, but there is little evidence of a continued loss from the 15 per cent layer to the 5 per cent layer. At the end of two years can 2 had not gone further toward equilibrium than can 1 had in the first 2 months, a difference due to the smaller moisture content in can 2, and possibly to the operation of gravity in can 1.

In can 3 there were three layers with 15 per cent, 10 per cent, and 5 per cent moisture respectively from top to bottom. In this can there was an opportunity for gravity to operate toward the establishment of equilibrium, which could be brought about only by the movement of moisture from the top layer to the bottom one through the middle layer, which was already at the average percentage for the can. In the first 2 months there was a movement which extended less than half way toward equilibrium. In the succeeding periods there was only a slight additional movement, involving an increase in the moisture of the 5 per cent layer at the expense of the central 10 per cent layer, with little effect on the upper 15 per cent layer. At the end of the first year the average of the six determinations was 10.1 per cent. The middle layer had returned approximately to its original content, and the top and bottom layers had gone a little more than half way toward equilibrium. The readings taken at the end of the second year are high, with an average of 12.3 per cent instead of 10 per cent, but they indicate the closest approach to moisture equilibrium shown in any member of the series, all six readings being much more nearly identical than in the determinations at the end of the first year.

In can 4 there were three layers with 5 per cent, 0, and 10 per cent moisture respectively from top to bottom. This can was planned to test the movements required to bring about equilibrium by the passage of water through a layer initially air dry. The readings taken at the end of the first 2 months showed an average of 7.1 per cent, which is much higher than the known average of 5 per cent, and the error appears to be chiefly in the readings for the top layer.

Throughout the history of this can there was a relatively small loss of moisture by the bottom layer, with some indications of a return of moisture to it from the middle layer. The middle layer fluctuated slightly but returned at the end of the second year to precisely the same readings obtained at the end of the second month. After May 1932 there was little change in the moisture in the top layer until November 1932. At the end of the second year there was an approximate equilibrium between the two upper layers, but the bottom layer showed no progressive change during the last 18 months of its history.

SUMMARY

Bodies of soil of known moisture content were firmly tamped into large garbage cans in two or three layers in each can, with differences of 5 per cent or 10 per cent between the continguous layers. The soil was sampled on alternate months for 1 year and again at the end of the second year. The soil used was an alluvial clay, or "adobe," with a water-holding capacity of 33.2 per cent.

In one of the four cans there was an approximation to equilibrium at the end of the second year, the extreme range of the readings being 11.8 to 13.0 per cent. In the other three cans a uniform distribution of moisture through the two or three layers was not attained.

The change in distribution of the moisture during the first 2 months was greater than the total of all change in the subsequent 22 months in all cases but one.

In some of the changes there is evidence of the influence of gravity. The individual layers of soil in a few cases showed the influence of an adjacent layer in the samples taken nearest it and a weaker influence in the sample or samples taken farther from it.

The evidence of these results, and of those obtained in previous work on the natural moisture changes of soil in place, indicates that the movement at the low percentages prevailing in desert soils is very small, at least in heavy soils. The only rapid changes in moisture content are the increases due to heavy rainfall and the decreases at the surface by evaporation or at lower levels by root absorption. When low moisture contents are concerned and small differences of content are involved, the action of capillarity in the slow distribution of water through the soil and in the establishment of moisture equilibrium is of little importance.

SOIL SAMPLING TUBES FOR SHALLOW DEPTHS

FRANK HEYWARD

Southern Forest Experiment Station, U. S. Department of Agriculture

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During the course of a study of forest soils in the Southeast, made by the Southern Forest Experiment Station, it has been necessary to collect several thousand samples from the upper portion of the soil profile. Three distinct types of soil tubes (fig. 1) were designed for the specialized sampling used in this study. These are as follows:

A: A tube for collecting samples for moisture determination of the 0 to 7-inch soil depth.
B: A tube for collecting a large number of cores in undisturbed field condition from the 0 to 6-inch soil depth of a size large enough to grow tree seedlings.
C: A tube for obtaining a large number of samples of constant volume from the 0 to 3-inch soil depth.

Since at least 200 samples have been collected with each tube, it has been possible to modify the original designs and thus correct imperfections. The tubes, as here described, have been found to be sturdy and easy to manipulate. They have been satisfactorily used to sample forest soils free from stones and varying in texture from fine sand to silt loam. For use in different regions or for sampling different depths it may be desirable to modify the general dimensions of the tubes as shown here.

TUBE A

Tube A is used for obtaining a core of soil in relatively undisturbed condition. After the core is collected, one half of the tube may be removed in such a manner that the soil core remains in the other half in a convenient position for removal in its entirety or in portions. The tube enables collection of a core approximately 2 inches in diameter and 7 inches long.

Operation. The tube is driven into the soil with a wooden mallet until the lower rim of the top touches the soil surface. The cutting edge is then 7½ inches beneath the surface. A hole is dug on one side to a depth of 6 to 7 inches with either a trowel or small spade, and the soil core is broken by tilting the top of the tube sharply toward the hole. The tube is removed from the soil, and the top is removed by disengaging the locking pins with a slight twist of the top. The tube is then held horizontally in one hand and the upper half removed with the other, which exposes the sample so that it can be removed as desired. Small grooves may be cut along the edges of the bottom half of the tube to designate particular depths beneath the surface, thus eliminating the use of a ruler in measuring depths of the desired portions of each core.

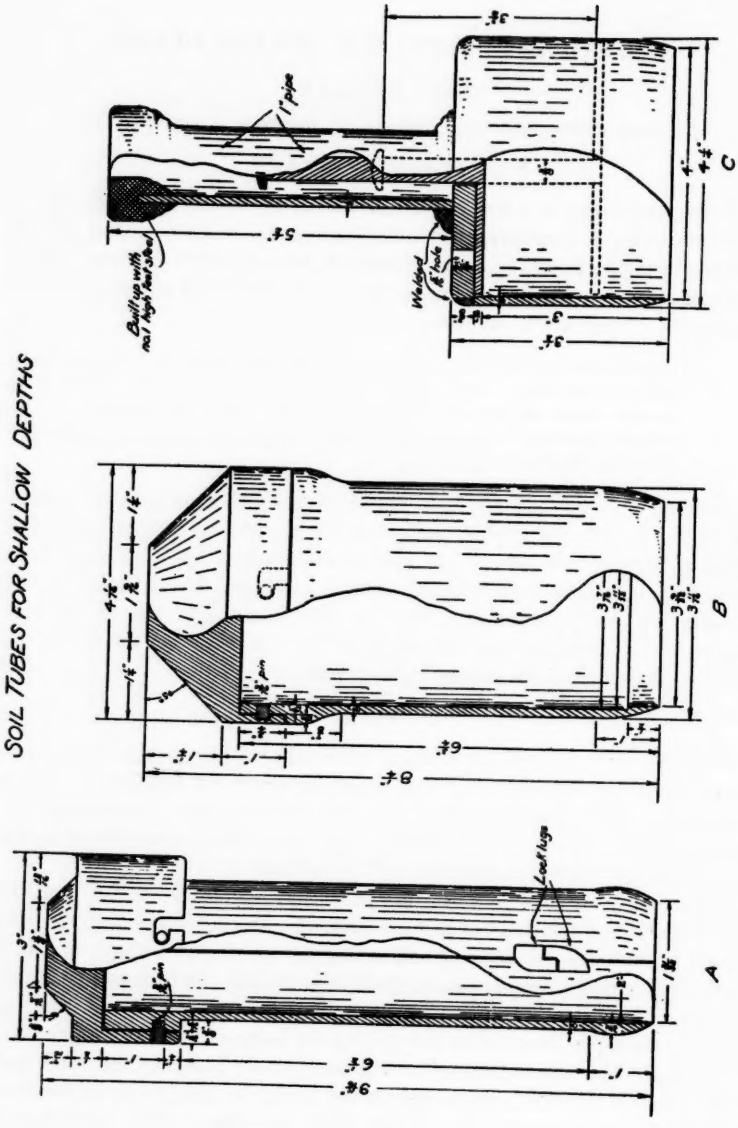
SOIL TUBES FOR SHALLOW DEPTHS
A
B
C
Leaf lugs
Weld on
Build up with hard high steel

FIG. 1

This permits very accurate sampling with respect to depth. Very dry soils cannot be sampled with this tube.

The effective sampling depth of the tube here described is 7 inches. An extra half-inch is allowed for loss when breaking off the soil core. If the tube is driven into the soil past the lower edge of the top, soil particles may work between the top and the tube proper and make removal of the top difficult. Therefore, it is best to consider the effective sampling depth of the tube from the cutting edge to the lower edge of the top. The top should fit tightly, as otherwise there may be movement of the separate halves of the tube.

Construction. The tube described here was made from standard 2-inch steel pipe. In order to have a cutting edge of smaller diameter than the rest of the tube, to prevent compaction of the soil core and to provide a slight enlargement on the outside to facilitate driving the tube into the soil, both interior and exterior of the lower portion of the tube were built up with high test welding steel. The tube was then mounted on a lathe and turned to required dimensions. The heavy $\frac{5}{16}$-inch upper portion of the tube was similarly constructed. The total cost of the tube, including hardening, was $8.

The upper portion of the tube must be considerably thicker than the $\frac{1}{8}$-inch wall of the lower portion to present a sufficiently strong bearing surface for the top, otherwise the rim will flatten out from constant pounding, and removal of the top will be difficult. The top is held firmly in place by means of two $\frac{3}{16}$-inch pins located on opposite sides of the upper portion of the tube. These engage with slots in the top. The slots should be large enough so that the top rests on the rim of the tube and not on the pins, which have little structural strength. The cutting edge should be case-hardened. It is also desirable, although not essential, to case-harden the upper edge which supports the top. The lock lugs are cut from $\frac{1}{16}$-inch steel and should be carefully welded on; these prevent the lower portions of the tube from separating. After being welded, they should be ground and smoothed on an emery wheel so that there are no projections on which roots or stones might catch and thereby bend or break the lugs.

TUBE B

This tube[1] was designed to provide a soil sample for seedling growth studies It was necessary to collect the sample in a field condition as undisturbed as possible. The adaptibility of the tube for additional studies, such as volume weight determination, percolation rate, and others requiring undisturbed soil, is obvious. The tube was designed to accommodate a 1-quart pasteboard carton, with cover removed, placed into the tube mouth down.

Operation. After the carton is inserted, the top of the tube is locked in place by twisting slightly to engage the two lock pins in their slots on opposite sides of the top. The tube is then driven into the soil to the desired depth with a wooden mallet. After the tube is dug from the soil with a trowel, the carton

[1] The writer designed this tube from suggestions received from T. S. Coile, who had made use of a similar one. Although several such tubes apparently have been used, no detailed description of them appears to have been published.

is removed and covered, the sample then being in an inverted position inside the carton. If samples thus collected are to be kept in the container for several months, as in a growth study,[2] or if they are to be used in soil moisture studies, it is necessary to paraffin the interior of the cartons to avoid deterioration of the carton or loss of moisture from the soil sample. Moisture content of soil does not influence sampling with this tube.

Construction. The cutting edge of the tube must be case-hardened. Unlike tube A, it is not necessary to harden or enlarge the bearing edge of the tube which supports the top, since the rim around the bottom of the pasteboard carton projects above the edge of the tube for a fraction of an inch and breaks the force of the blow on the tube. The pasteboard rim is slightly flattened, but this neither disturbs the soil sample nor seriously weakens the carton. Since both tube and top are driven into the soil, a somewhat different design was used from that of tube A, as may be seen in figure 1. The tube and top were turned from solid blocks of cold rolled steel. The approximate cost, including hardening, was $10.

Should it be desirable to use either a ½-pint or a 1-pint pasteboard carton in the tube, this may readily be accomplished by turning out on a lathe a wooden cylinder of proper diameter to slip easily into the tube and of proper length to fill the space between the bottom of the carton and top of the tube. The sample is then obtained as already described for the larger sized carton.

TUBE C

Tube C was designed to provide a rapid means of collecting samples of constant volume. Samples collected with the tube here represented, 4 inches in diameter and 3 inches in height, afforded a convenient means of volume weight determination, since, as a constant volume of soil was always obtained, only the oven-dry weight was needed. The sampler consists of a tube and a plunger for forcing out the soil.

Operation. The tube is driven into the soil until the plunger rests against the top. The two $\frac{5}{16}$-inch holes, on opposite sides of the top, afford a ready means of observing the position of the plunger. The tube is then dug from the soil with a trowel and the superfluous soil carefully cut off with a long-bladed knife so that the soil surface coincides with the level of the cutting edge. The soil is removed from the tube by inserting a metal rod (a 60-penny spike with the point sawed off is excellent) into the hollow handle and driving it against the stem of the plunger, thus forcing the soil out of the tube. Prior to the collection of each sample, the tube should be well shaken so that all soil particles which pass by the edges of the plunger are removed. This is an important precaution when sampling moist soils. Moisture content of the soil being sampled does not affect operation of this tube.

Construction. This tube may be turned out of ordinary steel pipe. The cutting edge should be case-hardened. The total cost, including hardening, was $4.

[2] In growth studies the upper side of the carton (actually the bottom) is cut off; the lid then becomes the bottom.

A SIMPLE METHOD OF FINDING THE LIME STATUS AND LIME REQUIREMENT OF SOILS, BASED ON REACTION WITH $CaCO_3$

AMAR NATH PURI AND A. S. VANSHYLLA

Irrigation Research Institute, Lahore (India)

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Lime status (L.S.) of a soil may be defined as the ratio expressing as percentage the exchangeable Ca actually present in the soil (Ca_1) over the exchangeable Ca the soil will have when brought into equilibrium with $CaCO_3$ (Ca_2), i.e.,

$$\text{L.S.} = \frac{100\ Ca_1}{Ca_2}$$

It might be stated at the outset that equilibrium with $CaCO_3$ does not represent the saturation of the acidoid with Ca ions. Lime status, therefore, should not be confused with the state of saturation of the soil. The advantage of using the $CaCO_3$ equilibrium point lies purely in its practical utility, for in nature no soil is more saturated with Ca than that point. The equilibrium point with $CaCO_3$ has already been suggested as the basis for the lime requirement of soils (1, 2, 3, 5). On account of the limited solubility of $CaCO_3$ its reaction with soils has an attractive simplicity, for a uniform condition can be easily maintained for all soils and no delicate adjustment is required for attaining the approximate equilibrium point.

The chief obstacle in the way of adopting the $CaCO_3$ equilibrium point as the basis for defining lime status has been the difficulty of estimating exchangeable Ca in the presence of excess $CaCO_3$. Since the single treatment methods of determining exchangeable Ca, developed by the senior author (4), have rendered such estimations extremely simple, it was of interest to explore the possibilities of using the newer methods for finding the lime status of soils.

EXPERIMENTAL

The starting point of this investigation was the potassium oxalate method of estimating exchangeable calcium in calcareous and carbonate-free soils (5). This method was slightly modified to suit the present conditions under which the soil suspension had to be shaken with $CaCO_3$. This consisted merely in using potassium oxalate-acetate-carbonate mixture of double the strength, every other detail remaining the same.

Some preliminary experiments were performed to study the conditions

under which equilibrium between $CaCO_3$ and soils could be attained. These will be described first.

TABLE 1

Speed of reaction between $CaCO_3$ and soil

TREATMENT	TIME OF SHAKING	EXCHANGEABLE Ca
	hours	*m.e.**
50 cc. H_2O	2	6.0
50 cc. H_2O + $CaCO_3$	2	11.0
50 cc. H_2O + $CaCO_3$	24	11.3
50 cc. 0.2 *N* KCl + $CaCO_3$	1	11.0
50 cc. 0.2 *N* KCl + $CaCO_3$	1.5	11.2
50 cc. 0.2 *N* KCl + $CaCO_3$	2	11.8
50 cc. 0.2 *N* KCl + $CaCO_3$	2.5	12.8
50 cc. 0.2 *N* KCl + $CaCO_3$	3	12.9
50 cc. 0.2 *N* KCl + $CaCO_3$	24	12.2
50 cc. 0.2 *N* KAc + $CaCO_3$	2	12.2
50 cc. 0.2 *N* KAc + $CaCO_3$	24	12.6

* Per 100 gm. soil.

TABLE 2

Speed of reaction between $CaCO_3$ and soil under partial vacuum

TREATMENT	TIME OF SHAKING	EXCHANGEABLE Ca
		*m.e.**
50 cc. 0.2 *N* KCl (10 gm. soil)	10 minutes	5.9
50 cc. 0.2 *N* KCl (15 gm. soil)	10 minutes	5.9
50 cc. 0.2 *N* KCl (20 gm. soil)	10 minutes	5.4
50 cc. 0.2 *N* KAc	10 minutes	5.5
50 H_2O + $CaCO_3$	10 minutes	9.3
50 cc. 0.2 *N* KCl + $CaCO_3$ (10 gm. soil)	10 minutes	9.9
50 cc. 0.2 *N* KCl + $CaCO_3$ (15 gm. soil)	10 minutes	10.2
50 cc. 0.2 *N* KCl + $CaCO_3$ (20 gm. soil)	10 minutes	9.2
50 cc. 0.2 *N* KCl + $CaCO_3$ (10 gm. soil)	1 hour	11.8
50 cc. 0.2 *N* KCl + $CaCO_3$ (10 gm. soil)	2 hours	9.4
50 cc. 0.2 *N* KCl + $CaCO_3$ (10 gm. soil)	3 hours	9.8
50 cc. 0.2 *N* KAc + $CaCO_3$	10 minutes	10.1
50 cc. 0.2 *N* KAc + $CaCO_3$	1 hour	9.8
50 cc. 0.2 *N* KAc + $CaCO_3$	2 hours	9.8
50 cc. 0.2 *N* KAc + $CaCO_3$	3 hours	10.0

* Per 100 gm. soil.

Speed of reaction between $CaCO_3$ and soil

A laterite soil from Dacca (Bengal) was chosen for these preliminary experiments. About 1 gm. of $CaCO_3$ was allowed to come to equilibrium with soil in the presence of water, potassium chloride, or, potassium acetate solution. Shaking was done occasionally with the hand for varying lengths of time.

After treatment with $CaCO_3$, the suspension was shaken with potassium oxalate-acetate-carbonate mixture, as described under "detailed description of the method," and exchangeable Ca was determined.

Another set of experiments was carried out in which the reaction between $CaCO_3$ and soil was allowed to take place under reduced pressure to facilitate the escape of CO_2. The results of the two sets of experiments are given in tables 1 and 2, from which the following conclusions may be drawn:

Equilibrium between $CaCO_3$ and soil suspension is attained fairly rapidly. One hour's shaking by hand at ordinary pressure and 10 minutes' shaking at reduced pressure are sufficient for the purpose.

The equilibrium point is not materially affected by allowing the reaction to take place in a solution of potassium chloride or potassium acetate instead of water.

The results are independent of the amount of soil taken; and 10 to 20 gm. of soil may be used for each determination.

The results in table 2 refer to a slightly different sample of the same soil, and the values are slightly lower than those in table 1. The difference, however, is well within the sampling errors which may normally be expected.

Detailed description of the method of finding lime status

Ten grams of soil is left with 50 cc. of water with and without $CaCO_3$ (about 1 gm.). The suspension is occasionally shaken by hand for 2 or 3 hours or may be left overnight. During this shaking the stopper is kept loose to allow the CO_2 to escape from samples to which $CaCO_3$ has been added. The reagent bottles can also be connected to an ordinary water pump and the reaction allowed to take place under reduced pressure when equilibrium can be attained in about half an hour.

When the reaction is complete the suspension is cooled to 10°C. and 50 cc. of the following solution is added: 0.2 *N* with respect to K oxalate, *N* with respect to K acetate, 0.03 *N* with respect to K carbonate.

The suspension is shaken by hand for about half an hour while the temperature is kept round about 10°C. It is then filtered through a dry, fluted paper, and 50 cc. of the filtrate is titrated with standard permanganate. The total decrease in the concentration of oxalate ion is equivalent to the exchangeable Ca, and the lime status (L.S.) is calculated as follows:

$$\text{L.S.} = \frac{100\ Ca_1}{Ca_2}$$

where Ca_1 = exchangeable Ca in the original soil, and Ca_2 = exchangeable Ca in the soil after being shaken with $CaCO_3$.

Lime status and lime requirement of soils

The lime requirement of a soil may be taken as equivalent to $(Ca_2 - Ca_1)$, i.e., the amount of Ca taken up by the soil from $CaCO_3$. We can express this value in tons per acre as follows:

One acre, six inches weighs 2,000,000 pounds, which is equal to 1000 tons (one short ton being equal to 2000 pounds). One milliequivalent of CaO is equal to 0.028 gm. Therefore, an increase of 1 m.e. of exchangeable Ca per 100 gm. of soil on shaking with $CaCO_3$ is equal to 0.28 tons of CaO per acre 6 inches. Lime requirement of a soil in tons per acre is equal, therefore, to $(Ca_2 - Ca_1) \times 0.28$. Of course this value has to be multiplied with a suitable factor according to the percentage of CaO in the given sample of lime; for instance, if liming is done with $CaCO_3$, lime requirement is equal to $(Ca_2 - Ca_1) \times 0.5$. It is interesting to note that the reaction between $CaCO_3$ and soil is very rapid; hence, liming with $CaCO_3$ should be as effective as with $Ca(OH)_2$. In table 3, lime status and lime requirements of some typical Indian soils are given. No claim is made as to the application of these values to field conditions except in the case of soil 6, which was taken from a field the lime requirement of which was actually determined by the author by growing a crop on it and was found equal to 1.3 tons per acre. The value of 1.62 tons per acre found by this method is sufficiently close to justify field trials with other soils.

TABLE 3

Lime status and lime requirement of soils

LAB. NO., P. C.	LOCALITY	pH	Ca_1	Ca_2I	Ca_2II	Ca_2III	L.S.	L.R.
							per cent	*tons**
3	Dharwar (Bombay)	7.64	51.2	52.0	52.4	55.6	98.5	0.224
6	Dacca (Bengal)	5.29	3.8	9.6	10.0	9.2	39.6	1.62
9	Malabar (Madras)	5.76	1.4	8.6	....	6.0	16.3	2.02
12	Tacklai (Assam)	5.84	2.8	7.6	8.2	6.8	36.8	1.34
14	Estate soil (Madras)	5.37	6.8	17.0	18.6	15.0	38.6	2.86
15	Shillong (Assam)	7.71	11.6	15.6	15.0	14.4	74.3	1.12
20	Lower Burma	5.64	1.9	5.5	4.9	2.9	34.5	1.01
25	Bhin soil (U. P.)	7.41	0.8	3.1	3.6	2.8	25.8	0.64
34	Gurdaspur (Punjab)	7.63	4.6	4.2	6.4	4.6	100	0
40	Umareth (Bombay)	7.65	7.6	9.6	10.4	8.8	79.2	0.56
45	Bihar	7.47	2.8	3.9	5.0	3.6	71.8	0.31
46	Baroda (Bombay)	7.63	38.2	43.2	42.2	....	88.4	1.40
49	Madhopur (Bihar)	6.33	10.8	13.6	15.6	13.6	79.4	0.78

Ca_1 = Exchangeable Ca in original soil (m.e. per 100 gm.).
Ca_2I = After treatment with $CaCO_3$ in water solution for 24 hours.
Ca_2II = After treatment with $CaCO_3$ in KCl solution for 24 hours.
Ca_2III = Ten minutes' shaking with water under reduced pressure.
L.S. and L.R. values on Ca_2I basis.
* Per acre 6 inches.

It is important that the distinction between lime status and lime requirement be clearly borne in mind. Lime status is a ratio and is somewhat similar to state of saturation (but should on no account be confused with it) of soil and as such can be used for comparing soils from different localities with regard to their fundamental properties. Lime requirement, on the other hand, is a quantity that shows the deficiency of Ca in a particular soil and is not fundamentally related to lime status. In other words, two soils having the same lime status may have entirely different values for lime requirement. When

the lime status of a soil is less than 100 per cent we can say that it may require lime, but just how much per acre, we cannot say. It is, therefore, advantageous when recording the values of lime status of soils to give the values for Ca_1 and Ca_2 in milliequivalents per 100 gm. of soil. This will enable anyone to calculate lime requirement values if required.

The proposed method of finding the lime requirement of soils has the merits of simplicity and ease of manipulation. It is based on a sound principle, and therefore values obtained are not dependent on the amount of soil, the time of shaking, or the strengths of solutions. The precautions to be observed are no more than those proposed for the analytical procedure for the estimation of exchangeable calcium.

SUMMARY

A method of determining the lime status and lime requirement of soils is outlined. It consists in the estimation of exchangeable calcium before and after treatment with $CaCO_3$, by the potassium oxalate method.

Within limits, the results obtained are independent of the amount of soil, the strength of solution, or the time of shaking.

Results with some typical Indian soils are given by way of illustration.

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THE RELATION OF CRYSTAL STRUCTURE TO BASE EXCHANGE AND ITS BEARING ON BASE EXCHANGE IN SOILS

W. P. KELLEY[1] AND HANS JENNY[2]

University of California

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The colloidal fraction of the soil contains a high percentage of the total exchangeable bases of the whole soil, but a considerable part of the Mg of the colloidal fraction is not replaceable in the ordinary sense of the term, and the same is true in some cases, at least, of Ca, K, and Na. However, the discovery by Hendricks and Fry (3) and by Kelley, Dore, and Brown (9) that soil colloids are composed, in considerable part at least, of crystalline material, and that the base-exchange capacity of soil colloids can be increased merely by reducing the natural size of the individual particles that compose the colloidal fraction (9), raises this question: Is there any fundamental difference between the exchangeable and the non-exchangeable bases of such materials? It is possible that the only essential difference between these two parts of the base-containing-constituents of soil colloids is merely a matter of particle size. If this is true it would seem to indicate that exchangeability of the bases depends on whether the ions happen to be located on the exposed surface of the colloidal particles and not necessarily, either that different kinds of compounds occur in the colloidal particles or that the bases are held to the particles by different kinds of attractive forces.

Kelley, Dore, and Brown reported that, corresponding to the increase in base-exchange capacity produced by grinding, there is a parallel increase in the replaceable Mg and K and also H ions in certain cases. They found this to be true both of soil colloids and of certain clay minerals.

The discoveries just alluded to tend to focus attention on crystal structure as such and on the base-exchange properties of pure minerals. They also raise three rather broad general questions: First, of what specific minerals are the soil colloids composed? Second, what determines the base-exchange capacity of the different classes of minerals? Third, are the exchangeable cations of minerals present as essential lattice constituents, and if so, what relation do they bear to the other components of the lattice?

It has long been known that the natural zeolites have pronounced base-exchange properties. In addition Lemberg (11) showed a half century ago that analcite can be converted into leucite, and *vice versa*, through base exchange;

[1] Professor of agricultural chemistry, University of California.

[2] Assistant professor of soils, University of Missouri.

Sullivan (17) and others have shown that a wide variety of the primary minerals undergo base exchange to a limited extent upon treatment with salt solutions. Despite these and other investigations, it is generally held that both the constituents of soils and pure minerals may be subdivided into two rather sharply defined classes; namely, those whose bases are replaceable and those whose bases are nonreplaceable.

Recently we have found that the base-exchange capacities of several minerals, some of which belong to one of the aforenamed classes and some to the other, tend to approach each other upon grinding the samples. For example, the exchange capacity of both orthoclase and muscovite can be raised to a comparatively high level (from 76 to 91.5 or more m.e. per 100 gm.) merely by grinding the sample to extreme fineness. What is still more surprising, the same is true of kaolinite and pyrophyllite. On the other hand, substances like quartz, colloidal SiO_2, precipitated $Al(OH)_3$, $Fe(OH)_3$, bauxite, and talc, have only low base-exchange power, as determined by the NH_4-acetate method, however long they may be ground.

According to modern concepts of crystal structure [Bragg, (1) Goldschmidt, (2) and Pauling, (14)], each Si ion in the silicates is surrounded by four closely packed O ions arranged in the form of a tetrahedron. The relative sizes of O and Si ions (Si = 0.8 Å, O = 2.7 Å) make possible a very close packing of four O ions around each Si ion. In quartz each O ion is a part of adjacent tetrahedra, which are so arranged that the negative charges of the O ions are just balanced by the positive charges of the Si ions. Consequently, quartz is electrically neutral, except on the surface, and contains no bases in the ordinary sense. In other silicates, such as the amphiboles, some of the O ions lie between two Si ions and some are attached to Si ions on one side only. Such minerals always contain enough metal ions to balance the remaining charges of the O ions. In certain of the alumino-silicates, such as the feldspars and zolites, the Al ions (1.1 Å) are also present in tetrahedra, being surrounded by four closely packed O ions. Since the Al ion bears only three positive charges, these minerals must contain additional cations (bases), sufficient to balance the excess negative charge of the Al tetrahedra. Potassium performs this function in orthoclase, biotite, and muscovite; sodium plays a similar rôle in albite, analcite, and natrolite; and calcium in anorthite and scolecite.

On the other hand, according to Pauling (15), each Al ion of pyrophyllite is surrounded by four O ions and two OH ions; in kaolinite each Al ion is surrounded by two O ions and four OH ions; that is, Al in these minerals has a coördination number[3] of 6. In these minerals the Al is said to occur in the octahedral position, and the positive charges of the Si and Al ions are just bal-

[3] Coördination number, as applied to crystals, refers to the number of ions bearing a given kind of charge, which immediately surround an oppositely charged ion. In the silicates the positively charged Si ions are always surrounded by four negatively charged O ions, whereas the Al ions of aluminosilicates are surrounded by either four or six O ions. Hence, the coördination number of Si is 4, whereas the coördination number of Al may be either 4 or 6.

anced by the negative charges of the O and OH ions; hence, these minerals contain no bases. However, the OH ions of kaolinite and pyrophyllite are essential parts of the lattice structure. Such minerals are said to be hydrous, that is, water is driven off at high temperatures. Upon complete dehydration a fundamental alteration takes place in their crystal structure, as is shown by X-ray examination.

CONDITIONS ESSENTIAL TO ION EXCHANGE

The two conditions which we consider essential to base exchange are; first, physical accessibility of the ion and, second, the strength of the attractive force by which the ion is held to the particle, that is, to the lattice. Further discussion of these points will be given later.

EXPERIMENTAL RESULTS

Feldspars. The feldspars are composed of so-called linked tetrahedra, consisting of both Si tetrahedra and Al tetrahedra. As is well known, the feldspars contain one equivalent of K, Na, or Ca for each Al atom. Since the Al tetrahedra contain, on the average, one excess negative charge, this is compensated for in orthoclase by the intake of a corresponding number of K ions at the time when the crystals are formed. Potassium ions are essential to the structure of orthoclase, but they are replaceable when brought into exposure by grinding. Similar statements can probably be made concerning Na in albite, Ca in anorthite, and Ca and Na in the soda-lime feldspars.

Table 1 gives the base-exchange capacities of several feldspars ground to different degrees of fineness. It will be noted that the exchange capacity, as measured by the neutral NH_4-acetate method, was increased markedly by grinding in a ball mill, especially in the case of orthoclase and albite. Unfortunately, we are not at present able to state the exact particle sizes of the samples used in this investigation, but it is certain that the average size of the particles was substantially reduced by the grinding process in the case of every mineral studied. The base-exchange capacities of the different feldspars, as reported in table 1, are not strictly comparable, because the different kinds of feldspars were ground under different conditions; but the different periods of grinding for a given feldspar, orthoclase for example, are strictly comparable. A rubber-lined ball mill and polished agate balls were used in all the grinding experiments. Therefore, the possibility of contamination of the samples through abrasion of ball mill parts was limited to silica.

Zeolites and permutites. As is well known, both the natural zeolites and the artificial permutites have high base-exchange capacity (see table 2). The Al ion of the zeolites is tetrahedral, and the same is probably true of permutite; consequently, these substances must contain additional cations (bases). In the zeolites the ordinary bases are located on exposed surfaces because these minerals have a honeycombed structure. The bases are arranged on the surface of intercommunicating internal cavities. These channels permit the

passage of ions, and therefore base exchange is physically possible on the interior of the crystals. Hence it is not necessary to reduce the size of the crystals of natural zeolites to extreme fineness in order to replace the bases. For example, we have found that practically all of the Na of analcite, a mineral related to the zeolites, can be replaced by K, as KCl, without excessive grind-

TABLE 1

Base-exchange capacity of feldspars

		m.e. per 100 gm.
Orthoclase	100 mesh	5.0
	Ground 24 hours	22.0
	Ground 48 hours	42.0
	Ground 120 hours	91.5
Albite	100 mesh	1.0
	Ground 48 hours	54.0
	Ground 72 hours	70.0
Labradorite	100 mesh	2.0
	Ground 72 hours	26.0
	Ground 96 hours	37.0
Oligoclase	100 mesh	2.6
	Ground 72 hours	27.0
Anorthite	100 mesh	2.0
	Ground 72 hours	24.0
	Ground 96 hours	33.0

TABLE 2

Base-exchange capacity of zeolites and permutite

		m.e. per 100 gm.
Zeolites:		
Scolecite	Ground moderately	209.3
Stilbite	Ground moderately	304.5
Natrolite	Ground 48 hours	74.5
Natrolite	Ground 72 hours	108.5
Permutite	Unground	225.0
	Ground 48 hours	225.0

ing of the sample. When this replacement has been effected, the product is an entirely different mineral, namely, leucite. This is in agreement with Lemberg's results.

On the other hand, permutite is commonly held to be amorphous; its specific surface is high. Consequently, its base constituents are accessible to the cations of solutions and are replaceable.

Thus the bases of zeolites and permutites conform to the first condition for replaceability, mentioned previously. Jaeger (7) has given a diagrammatic representation of the crystal structure of ultramarine, a mineral that is related to the zeolites, in which he showed the replaceable Na ions and H_2O molecules on the interior surface of the crystal.

The zeolites represent very much more open packing of the tetrahedral ionic clusters than do the feldspars. The latter are, accordingly, much harder minerals, and, in turn, much more drastic grinding is necessary to bring the bases into exposure.

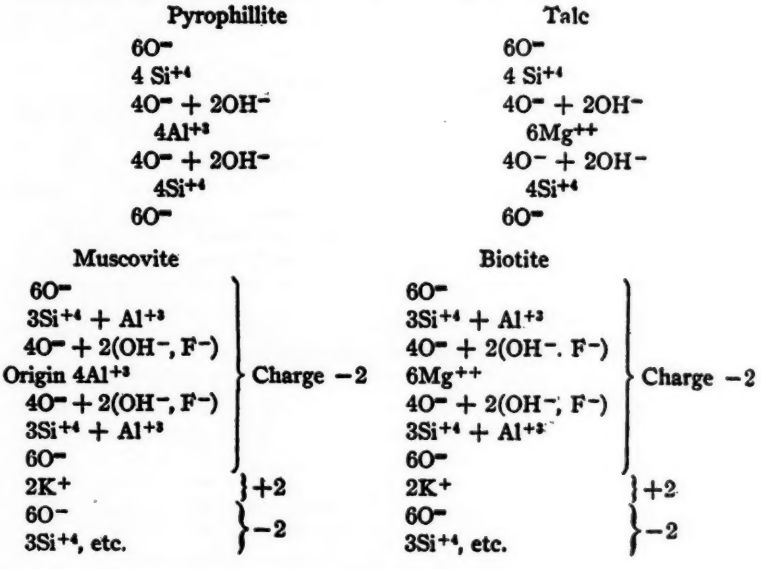

FIG. 1. SEQUENCE OF ATOM-PLANES ALONG THE PSEUDO-HEXAGONAL AXIS OF PYROPHYLLITE, TALC, MUSCOVITE, AND BIOTITE
Reproduced from Pauling (15)

The micas. As is well known, the micas are platy minerals. They cleave most readily along one axis. According to Pauling, (15) the crystal structure of the micas is made up of a series of planes of ions as shown in figure 1. It will be noted that the K ions all occur on the cleavage planes. It follows then that, were it possible to separate the sheets of mica down to the thickness of a single lattice package, all of the K ions would be exposed. Grinding tends to do this; hence it increases the base-exchange capacity, as shown in table 3.

Biotite contains Mg ions as essential lattice constituents. According to Pauling, the Mg ions of biotite bear the same relation to O and OH ions as the octahedral layer of Al ions in muscovite (see figure 1). Moreover, the Mg-

containing octahedra of biotite are similar to those of talc and brucite. When finely ground, is this Mg replaceable? We have found that relatively much Mg can be extracted from finely ground biotite by neutral NH_4 salt solutions, but that the amount of NH_4 absorbed from the salt solution is equivalent only to the K that is removed from the sample (see table 4). Further reference to this point will be made in connection with the discussion on talc.

Talc. According to Pauling, (15) each Mg ion in talc is surrounded by four O and two OH ions. The layers of lattices are held together by stray electrical forces, as contrasted with muscovite and biotite in which the layers are held together by K ions (see figure 1). Talc is a relatively soft mineral and is

TABLE 3

Base-exchange capacity of the micas

		m.e. per 100 gm.
Muscovite	100 mesh	10.5
	Ground 72 hours	76.0
Biotite	100 mesh	3.0
	Ground 48 hours	62.0
	Ground 72 hours	72.5

TABLE 4

Effect of ammonium acetate on the micas

		BASES EXTRACTED BY NH_4 ACETATE		ABSORBED
		Mg	K	NH_4
		m.e.	*m.e.*	*m.e.*
Muscovite	100 mesh	Tr.	9.1	10.5
	Ground	Tr.	52.5	48.3
Biotite	100 mesh	14.3	8.2	8.8
	Ground	113.0	60.0	62.0

readily ground to extreme fineness. When it is thus ground, we have found that NH_4 salt solutions are able to extract large amounts of Mg, and at the same time the substance appears to undergo decomposition. This decomposition may be viewed in different ways: First, we may assume that NH_4 ions replace those Mg ions which are present on the surface of broken octahedra, with the resulting formation of NH_4 silicate, which is an unstable compound. Or, second, we may say that the NH_4 ions first replace Mg ions, and then the NH_4 ions are replaced by H ions of the solution, thus converting the substance into silicic acid; this, of course, is equivalent to saying that NH_4 silicate hydrolyzes. Or, third, we may look upon the case as follows: When NH_4 replaces the octahedral Mg ions, the NH_4 ions find themselves attached to O and OH ions,

which is an unstable arrangement. Whatever be the correct explanation, the fact that the Mg of biotite and talc behaves similarly toward NH_4 salt solutions is in harmony with Pauling's conclusions regarding the similarity in the crystal structure of these minerals.

The chlorites, pyroxenes, and amphiboles. Pauling (16) has shown that, from a crystal structure standpoint, the basic igneous minerals are combina-

TABLE 5

The effect of ammonium acetate on talc, chlorite, bauxite, and quartz

		BASES EXTRACTED BY NH_4 ACETATE		ABSORBED
		Ca	Mg	NH_4
		m.e.	*m.e.*	*m.e.*
Talc	100 mesh	Tr.	9.8	Tr.
	Ground	Tr.	219.0	Tr.
Chlorite	100 mesh	5.0	32.0	6.0
	Ground	35.0	88.0	34.5
Prochlorite	60 mesh	Tr.	12.5	Tr.
	Ground	Tr.	243.0	50.0
Bauxite	100 mesh	Tr.	Tr.	Tr.
	Ground	Tr.	Tr.	Tr.
Quartz	100 mesh	0	0	Tr.
	Ground	0	0	2.0

TABLE 6

Base-exchange capacity of kaolinite and pyrophyllite

		m.e. per 100 gm.
Kaolinite	100 mesh	8.0
	Ground 48 hours	57.5
	Ground 72 hours	70.4
	Ground 7 days	100.5
Pyrophyllite	100 mesh	4.0
	Ground 48 hours	72.5
	Ground 72 hours	92.0
	Ground 7 days	158.5

tions of the structures of mica and brucite. Since Mg in the brucite-like octahedral arrangement splits off upon treatment with NH_4 salt solution without the absorption of NH_4, and since Mg is the predominant base of these minerals, their base-exchange capacities, as measured by the ammonium acetate method, should be relatively low (see table 5).

Pyrophyllite and kaolinite. Since pyrophyllite and kaolinite contain none

of the common bases, it is especially interesting to find that, upon being ground to extreme fineness, they possess high cation-exchange power (see table 6). We believe that this exchange power is traceable to the H ions of the crystal lattice of these minerals.[4]

From the standpoint of H-ion replacement two types of OH planes are of special significance. First, a plane of OH ions immediately on the exposed surface of a lattice package which is arranged in the following manner:

H	H	H	H	H	H	(hydroxyl plane)
O	O	O	O	O	O	

Second, a subsurface OH plane, which is covered by a network of O ions, as illustrated by the following:

O	O	O	O	O	O	(oxygen plane)
H	H	H	H	H		(hydroxyl plane)
O	O	O	O	O		

The important feature of the second type of arrangement lies in the fact that the H ions of the OH plane are accessible through the meshes of the superimposed O network. Each of the two surfaces of pyrophyllite lattice packages consists of the latter type of plane, whereas kaolinite contains both types. Just how readily these H ions can be replaced is not known at present; one would expect, however, that they are held rather tightly and that alkaline solutions would be required to produce efficient exchange.

Grinding may split these crystals parallel to the basal planes or vertical to them. In the first case new planes containing H ions would become exposed; in the second case the octahedral groups of the lattice (10, fig. 14) would be broken and the bond strength between O and H be altered.

The bentonites and soil colloids. The published analyses of bentonite always show more or less Ca and Mg and usually small amounts of Na and K. In our experience, practically all the Ca, K, and Na of the more common types of bentonitic clays are replaceable, provided the necessary steps are taken to separate the clay constituents from fragments of associated minerals. On the other hand, only a minor percentage of the Mg is replaceable, but additional amounts of Mg become either replaceable or extractable after the mineral has been ground in a ball mill. As Kelley, Dore, and Brown (9) pointed out, and as shown in table 7, the base-exchange capacity of a given bentonite, and also of soil colloids, can be markedly increased by grinding the sample.

Exchange power of betonites and soil colloids. At present we cannot say what is the upper limit of the base-exchange capacity of the bentonitic clays and soil colloids. We have been able to raise the base-exchange capacity of one sample of bentonite from 126 to 238 m.e. per 100 gm., and it is highly probable that further grinding would produce still further increase. With one Yolo

[4] Direct experimental proof that the exchange power of ground kaolinite and pyrophyllite is due to H ions of the lattice will be published elsewhere.

soil colloid we have raised the exchange capacity from 67 to 166 m.e. In the case of the Cecil colloid the capacity was increased from 17 to 151 m.e. and the Redding soil colloid was affected similarly. With the Yolo colloid the increased exchange capacity appears to be due chiefly to Mg and K ions, whereas in the Cecil and the Redding it was occasioned mainly by H ions brought into exposure by the grinding process.

TABLE 7

*Base-exchange capacity and pH of bentonite, beidellite, talc, and soil colloids as affected by grinding**

		m.e. per 100 gm.	*pH*
Bentonite No. 2	1 micron	126.0	7.3
	Ground 72 hours	238.0	9.1
Beidellite	1 micron	50.0	6.4
	Ground 48 hours	200 5	7.6
Talc	100 mesh	Tr.	6.9
	Ground 48 hours	Tr.	8.9
Yolo soil colloid	1 micron	67.0	7.3
	Ground 48 hours	166.0	7.3
Cecil soil colloid	1 micron	17.0	7.2
	Ground 48 hours	151.0	5.4
Redding soil colloid	1 micron	35.0	6.6
	Ground 48 hours	122.5	5.5

* Before being subjected to the grinding process, the samples of bentonite, beidellite, and soil colloids were Ca saturated by leaching with neutral Ca acetate solution.

ON THE NATURE AND STRENGTH OF ATTRACTION FORCES

Goldschmidt and Pauling have shown that it is possible to explain many of the features of alumino-silicates by assuming that the atoms are electrically charged spheres (ions) and that they are held together with electrostatic forces of the Coulomb type. We believe that the same forces are active in base-exchange reactions, especially if ions of large size, such as K, Cs, or hydrated Li and Na, are involved. For some ions, such as the H ion, and possibly Be and Mg ions also, a transition to electron-pair bonds appears plausible.

When lattice ions become exposed on the surface, they experience greater freedom of movement and oscillate over greater distances; thus they may be replaced by other ions according to the mechanism proposed by Jenny (8). The term "surface dissociation of ions," which is frequently used in soil literature, does not appear appropriate, except perhaps for the H ion, because the bases are considered to be already dissociated in the solid state.

The behavior of the H ion is particularly interesting. According to our

viewpoint it lies opposite an O ion (in exceptional cases opposite an OH ion) in such systems as are represented by hydrous, crystallized alumino-silicates. The feldspars do not contain OH ions, but upon hydrolysis or electrodialysis the K, Na, or Ca ions become replaced by H ions, and then H ions are attached to O ions. This viewpoint leads directly to a parallelism with many organic substances; proteins, for example, also show base exchange and they also have an exchangeable H ion associated with an O ion (C(=O) – OH group). The activity of these exchangeable H ions depends upon the intensity of the attraction between H and O, which in turn is influenced by the neighboring lattice ions. We believe that the different acidities of many soil colloids and minerals can ultimately be explained by the nature of the attractive forces acting on various parts of the crystal lattice, such as the planes, corners, or edges.

DISCUSSION

From the foregoing it follows that the base-exchange power of crystalline minerals may be explained on the basis, first, of accessibility and, second, of the strength of the attractive force by which the bases are held to the lattice. More precisely, it may be said that, with the exception of the bases that have replaced H ions from the broken lattices of the hydrous minerals, only those metallic cations which perform the function of balancing the excess negative charges of the tetrahedral groups (and possibly the negative charge of the octahedra in exceptional cases) are reversibly replaceable by NH_4. With the platy minerals of the mica group, these metallic cations occur on the surface of the cleavage planes; in the zeolites and feldspars they occur on the surface of internal cavities. These cavities are large enough in the zeolites to permit access to the ions of a solution, whereas with the feldspars the structure is more compact; the bases are similarly situated in the lattice of both types of minerals.

Although we have not as yet investigated all the various classes of silicates, it seems probable that the K and the Na of all of them are essentially replaceable, provided the particles can be made small enough to permit physical access to these ions. The same may be true of Ca, but, as has been indicated, the case is considerably more complex for Mg. The octahedral Mg is probably not stoichiometrically replaceable by the alkalies or NH_4, at least not when OH ions constitute parts of the octahedra. On the other hand, Mg ions can readily replace other replaceable cations, and the process is known to be reversible.

Recently, van der Meulen (13) pointed out that the various silicates may be subdivided into three different groups: First, those containing no Al; second, those containing Al with coördination 6; and third, those containing Al with coördination 4. He claims that the first two groups have practically no base-exchange property but that the third group has definite base-exchange property. In the group which contains no Al there are such well-known minerals as

quartz, talc, and wollastonite. In the group containing Al with coördination 6, van der Meulen lists kaolinite and cyanite. He holds that the cation-exchange power of these minerals is practically zero. However, to his list we must add pyrophyllite and probably montmorillonite and beidellite; but the last two of these have extremely high base-exchange power in their natural condition, and the same is true of finely ground kaolinite and pyrophyllite. As minerals the aluminum of which has a coördination 4, van der Meulen names several zeolites, and also orthoclase and other feldspars, the micas, and several other minerals.

Van der Meulen points out that, although the open structure of the zeolites makes possible an exchange of cations on the interior of the crystals, this is not true of a feldspar crystal. He states, "If, however, the crystal is very finely pulverized a great number of Al atoms with coördination value 4 are at the surface of the particle and become accessible for exchanging cations." Although careful reading of van der Meulen's paper shows that his view is essentially the same as ours, in so far as the exchange property of the feldspars and zeolites is concerned, the statement just quoted is inaccurately phrased, because it attributes the cation-exchange power to the exposed Al atoms themselves. It is more correct to say that the negative charges imparted to the lattice by virtue of tetrahedral Al ions are responsible for the fact that orthoclase and the micas *contain* K ions and that these K ions are replaceable upon exposure. The K ions are directly attached to O ions of the Al tetrahedra in the zeolites, orthoclase, and the micas.

When kaolinite and prophyllite are finely ground, relatively many OH ions of the lattice become exposed because breaks are produced either across the octahedral layers or parallel thereto. We believe that the cation-exchange power of these ground minerals is due in large part, at least, to the OH groups that are exposed by breaks across the octahedral layers, but it must be admitted that as yet we have been unable to prove definitely just where the active exchange spots are located. We have found, in agreement with other investigators, that relatively coarse particles of these minerals (100 mesh) have only low cation-exchange power (4 to 8 m.e.). Even in this case the cation-exchange power is probably due to H ions on the surface of broken lattices of the crystals.

Hofmann, Endell, and Wilm (5) have published a diagram, reproduced as figure 2, that is intended to show the seat of the exchangeable ions on a clay crystal. According to this model, the cations are held by broken bonds on the edges of the Si-O planes. At first sight this viewpoint is very appealing, but upon closer examination a serious difficulty arises. Suppose we take a clay crystal containing an extensive Si-O plane, and break it, in the air, into a large number of small pieces. Tetrahedra will be broken and many free bonds will necessarily appear on the broken surfaces, but, up to this point, no replaceable bases will be present, since there were none in the original material. Hofmann, et al. hold, it is presumed, that these are adsorbed by the free val-

ences when the crystal fragments come into contact with a solution containing cations (K, Ca, H, etc.). It is just here that the difficulty comes in. If the broken bonds should bind cations from the solution, what would happen to the remaining anions in the solution? If their hypothesis is valid, then when the clay fragments were removed from the solution more anions than cations would be left in the solution, but such a system cannot exist, for it violates the law of electrical neutrality. In other words, a solid cannot adsorb cations from solutions without an exchange process or an equivalent adsorption of anions. The model of Hofmann, et al. (fig. 2) does not satisfy either of these two conditions.

Theoretically, the following modification would overcome the objection raised. The broken bonds might polarize and adsorb water molecules, which dissociate on the clay surface into OH and H ions. The latter then act as

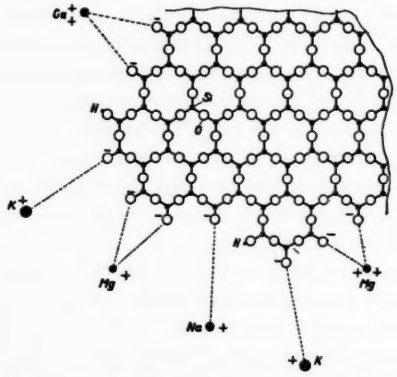

FIG. 2. DIAGRAMMATIC REPRESENTATION OF A Si-O LAYER OF A CLAY CRYSTAL WITH CATIONS ATTACHED TO THE FREE O VALENCES ON THE EDGES OF THE BROKEN LATTICES
Reproduced from Hofmann et al. (5)

replaceable cations. Experiments to test this hypothesis, however, have thus far given practically negative results (see the data for quartz, table 5). At present we must conclude that the bulk of the exchangeable cations of the clay minerals are not held by the broken bonds on the edges of the Si-O planes.

Since the bentonitic clays contain OH ions as lattice constituents and since their individual particles are extremely small, we believe that, with the possible exception to be noted presently, the cation-exchange power of the natural bentonites is due to exposed OH groups of the crystal lattice. With natural bentonites the H ions of these exposed OH groups have already been replaced in the state of nature, and for this reason the bentonites are usually saturated with exchangeable metallic cations. Upon grinding, additional OH groups become exposed, and thus the exchange capacity is increased.

Hofmann, et al. (5) and Marshall (12) have suggested that Mg and Fe may

occupy a position in the bentonite (montmorillonite-like) crystals, similar to that of octahedral Al, that is, surrounded by O and OH ions (10, fig. 14). As Marshall (12) suggests, this would either produce a mixed hydrargillite-brucite structure, in which case the lattice would acquire one negative charge for each Mg ion thus introduced and therefore additional cations would be required to balance these negative charges, or else it would produce a brucite-like structure.

Either of these alternate modes of substitution of Mg for Al would introduce Mg ions into the octahedral positions. Upon grinding material of this kind, it is reasonable to suppose that more or less of such Mg ions would become exposed, as in the case of ground biotite and talc, but these Mg ions ought not to be stoichiometrically replaceable by NH_4. However, they should be extractable by NH_4 salt solutions. It is interesting to note that the pH of bentonite is affected by grinding (see table 7) very much as is talc, a mineral the Mg of which certainly occupies the octahedral position. It is probable that the Mg ions, brought into exposure by breaks across the octahedra, hydrolize and thus produce increases in the pH.

On the basis of data obtained with samples of bentonitic clays from several different localities in North America, there appears to be some relation between content of nonreplaceable Mg and base-exchange capacity. For example, Vanselow has found that Wyoming bentonite from the type locality contains approximately 1.6 per cent nonreplaceable MgO and has a base-exchange capacity of 86 to 88 m.e. per 100 gm. On the other hand, another type of bentonite obtained from two different localities, namely, Otay, California, and Goldfield, Nevada, contains about 4.60 per cent nonreplaceable MgO and has a base-exchange capacity of about 107 m.e.[5] These differences in base-exchange capacity are less than one-third what they should be if each Mg ion imparts a negative charge to the exposed surface of the particles.

Marshall (12) has also concluded that Al can replace Si in the lattice of the clay crystals, as well as be replaced by Mg, Fe, and Ti. Should one-fourth of the Si ions be replaced by Al ions, this would produce a structure closely analogous to that of muscovite minus its K ions (assuming that the ideal structure of montmorillonite by Hofmann, et al. is essentially correct). The substitution of Al for Si, however, would certainly result in one negative charge on the lattice for each Si ion that is replaced. Just as in the micas, these negative charges would have to be neutralized by the absorption of cations, and such cations might be held on the interplanar surfaces of the lattice. Wherever they occur, whether on the surface of the lattice framework or on its interior, these cations would be replaceable upon exposure.

It is possible that the substitution of Al for Si is involved in certain Yolo soil colloids of California but that the replacement of Al by Mg plays an insignificant part in them. We have found, for example, that when a sample of Ca-

[5] The authors are grateful to Dr. Vanselow for these data.

saturated Yolo colloid is ground, additional Mg and K ions become replaceable, but that the pH is not materially altered, indicating that this colloid does not contain significant amounts of octahedral Mg. Preliminary X-ray examination of this colloid has failed to show any relation between the content of adsorbed water and the X-ray spectrograph. In this respect it appears to be similar to the unidentified clay mineral discussed by Jacob, et al. (6).

The ideas developed in the foregoing paragraphs suggest that the bentonitic types of clays are structurally related to the micas, and it is interesting to note that their properties are similar in several respects. It must be admitted, however, that the structure, as proposed by Hofmann, et al. is only a first approximation. Further investigation may necessitate modifications in their lattice structure. It is important to bear in mind that the determination of the structure of fine-grained substances, like the bentonitic and other clays, is difficult. Only powder X-ray spectrographs of these minerals have as yet been made and these are commonly difficult to interpret.

In collaboration with Mr. W. H. Dore, we have verified the conclusion of Hofmann, et al. (4), that the interplanar distances between lattice packages of the bentonitic clays vary according to water content. More recently Jacobs, et al. (6) have found that certain soils contain minerals similar to kaolinite, other soils contain minerals similar to montmorillonite, and still others contain an undetermined crystalline clay mineral. These conclusions are in harmony with those of Marshall (12) which were based on calculated substitutions within the lattice of different samples. They also agree with the dehydration data of Kelley, Jenny, and Brown (10) and with unpublished X-ray data obtained in connection with this investigation.

Reference again to the effect on pH, produced by grinding (table 7), will show that, whereas Ca-saturated bentonite and talc become more alkaline when ground, the Ca-saturated Cecil and Redding soil colloids become more acid. On the other hand, the pH of Yolo soil colloid is altered but little by grinding, whereas that of beidellite is increased by grinding to an intermediate degree. When these facts are considered in conjunction with (*a*) the dehydration curves of these materials (10), (*b*) the unpublished X-ray and chemical analyses, and (*c*) the data showing the effect of grinding on the content of replaceable Ca, Mg, K, Na, and H ions, it is difficult to avoid the conclusion that the Yolo colloid is more like beidellite than montmorillonite, though not identical with beidellite, and that the Cecil and Redding colloids are utterly different from either montmorillonite or beidellite, in fact, they seem to resemble the kaolinitic minerals.

It is highly probable that soil clays embrace a complex series of isomorphous minerals and that certain soils contain one general type of clay mineral, whereas other soils contain a second or a third type. The type actually predominating in a given mature soil would be expected to be that which is most stable under the conditions prevailing in that soil. On the other hand, it seems reasonable to suppose that immature soils might contain variable mixtures of clay minerals. At any rate, all of these clay minerals have more or less base-exchange power.

It follows, then, that no one single substance is responsible for base exchange in all soils. Jacob, et al. (6) have concluded that the base-exchange property of soils is not due to zeolites or permutite-like substances. Kelley, Dore, and Brown (9) drew similar conclusions in 1931.

Finally, we wish to emphasize the fact that the authors consider the views developed in this paper to be essentially tentative. We believe that the OH of the lattice of clay minerals is an important source of their potential cation-exchange power, but it does not follow that the OH group is the sole cause of their exchange power. Should further investigation definitely establish that Al replaces Si in the clay minerals, and also that Mg replaces more or less Al, the negative charges thus introduced on the lattice would certainly necessitate the introduction of cations, and such cations would probably be potentially replaceable. As Marshall has pointed out, there are several other possible substitutions which would also influence the exchange power. In the present state of knowledge it is not possible to decide definitely between these possibilities.[6]

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STUDIES ON PODZOLS AND BROWN FOREST SOILS: III

KARL LUNDBLAD

Svenska Mosskulturföreningen, Jönköping, Sweden[1]

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The first part of this paper dealt with the acid-oxalate method of Tamm, used to demonstrate the differences between podzols and brown forest soils (4). The second part showed that the amphoteric properties of the soil colloids may be used for studies of the soil forming processes and that they give reliable information about the differences between the soil types investigated (5). It will now be shown that dye adsorption can also be used as a means of characterization. The profiles studied are the same as those used in the previous parts of the paper (4, p. 146–148).

ADSORPTION OF ACID AND BASIC DYES

It has long been known that colloids are able to "adsorb" organic dyes of different kinds. Many of the common color reactions used in microscopical work are based on this ability.

The first attempts to determine the amounts of colloids in soils through their adsorption of dyes seem to have been made by Endell and by Ashley. Endell's method—here quoted from Hissink—was very similar to the common way of dyeing microscopical preparations (2, p. 38). Ashley's method—here quoted from Stremme—is colorimetrical and similar to the one now employed by the author (9, p. 26). Aarnio and Stremme found that methylene blue was a suitable dye but that the other dye solutions tried were discolored in the presence of lime carbonate (9; 10, p. 27).

The adsorption of methylene blue has since been used by several investigators. A real explanation of the reaction between dye and colloid was first given by Mattson (6, 7, 8). Stremme anticipated the conception of the soil colloids as ampholytoids when writing about the methylene blue adsorption: "In Böden mit saurer Reaktion könnten Tonerde und Eisenoxyd eher als Basen wirken während sie in Böden mit alkalischer Reaktion eher Säuren sein könnten" (9, p. 31). Mattson's results concerning the adsorption of methylene blue can be summarized as follows (8, p. 381): The methylene blue cation is completely adsorbed over the entire range on the electronegative side of the isoelectric point; therefore, the quantity adsorbed is directly proportional to the amount of colloid when the resulting complex is isoelectric. The quantities thus adsorbed by different colloids are a direct measure of their exchange capacity. The methylene blue cation displaces other cations but is not dissociated by the particles; therefore, the complex is isoelectric when the other cations are displaced. The adsorption proceeds beyond the isoelectric point but becomes

[1] The laboratory work involved in this study was done by the author in the laboratory of Dr. Sante Mattson during a stay as Cook-Voorhees Research Fellow at the New Jersey Agricultural Experiment Station October, 1931–September, 1932 [see acknowledgment in the first part of this paper (4)].

more and more incomplete as the positive charge increases. The fact that this dye is totally adsorbed up to the isoelectric point suggests a possibility of studying the soil colloids both qualitatively and quantitatively.

If the theory of isoelectric weathering is true we should expect a high adsorbing capacity for methylene blue in the A_2 horizon of a soil of the podzol type because the acid weathering should leave there a colloid complex rich in more or less strong acidoid groups. The adsorbing capacity should then decrease through the B and C horizons where colloids richer in ampholytoid groups, such as sesquioxides, and poorer in acidoid groups have been deposited as a result of the weathering. But the adsorbing capacity—though in the strict sense of the word a qualitative property—depends also on the quantity of colloids present, and if the percentage of colloids is high the adsorbed quantity of dye can be larger than that in a soil of a relatively much stronger acidoid character but poorer in colloidal material.

The basic dye night blue was used for some of the experiments though later it was abandoned for methylene blue because of some difficulties in its use. In the experiments with cataphoresis in night blue solutions, the measurements were made in the way previously described. The results are shown in table 7.

From the results it is apparent that the total adsorption continues to the isoelectric point—the fact that, in some cases, a slight coloration is observed at low concentrations of the dye is accounted for by an incomplete flocculation. On the other side of the isoelectric point additional dye is adsorbed, as found from other experiments, but the percentage of dye taken from the solution decreases with increasing concentrations until a point is reached where an increase in concentration does not materially affect the adsorption. The amounts of dye adsorbed at the isoelectric point are (partly interpolated values) in A_2, 0.90; in B_1, 1.30; in B_2, 0.34; and in C_2, 0.13 mgm. per gram of soil. Thus we find a higher adsorption in B_1 than in A_2 though the acidoid character of the colloids must be more pronounced in A_2. This means that the quantities of colloids present veil their qualitative properties. The pH values of the different isoelectric systems were about as follows: A_2, pH 4.5; B_1, pH 4.7; B_2, pH 5.0; and C_2, pH 5.3. The quantities of dye required to render the soils from the various horizons isoelectric are, with the exception of B_1, very closely proportional to their combining capacities at pH 7, as given in table 6 and in figure 10 of part II (5). The fact that the value of 1.30 mgm. in the case of B_1 is, in proportion to the combining capacity, so much lower than the other values may be accounted for by the relatively low pH of 4.7. At this pH the strongly basoid B_1 cannot be expected to combine with very many cations, even those of a basic dyestuff.

This experiment shows that adsorption of basic dyes may possibly give a false impression of the quality of the colloids in a soil profile and therefore no certain idea of the type of soil forming process, just as determinations of the base exchange only are not conclusive. It was previously suggested that

the base exchange determinations be combined with determinations of the anion exchange capacity. Just as this property would give true information about the soil forming process in the case of soils formed by the acidoid type of weathering, so it is quite natural that an acid dye would give the same re-

TABLE 7

Cataphoresis of soil samples from a podzol profile, number 5, in night blue solution

2.5 gm. of soil in 25 cc., measurements after 24 hours

NIGHT BLUE	CATAPHORESIS	COLOR OF SOLUTION	CATAPHORESIS	COLOR OF SOLUTION
	A_2 horizon		B_1 horizon	
mgm.	*μ/sec., 1 volt/cm.*		*μ/sec., 1 volt/cm.*	
0	−3.19		−1.26	
0.25	−3.03	Very light blue	−1.08	Nearly colorless
0.50	−2.75	Very light blue	.....	
0.75	−2.52	Nearly colorless	−1.08	Colorless
1.00	−2.47	Nearly colorless	.....	
1.25	−2.33	Colorless	.....	
1.50	−2.02	Colorless	.....	
1.75	−0.95	Colorless	−1.01	Colorless
2.00	−0.38	Colorless	−0.87	Colorless
2.25	− slight	Colorless	−0.67	Colorless
2.50	+1.51	Blue	.....	
2.75	.....		−0.43	Colorless
3.00	+2.52	Blue	−0.38	Colorless
3.25	.....		±0.00	Colorless
3.50	.....		+0.38	Very light blue
4.00	+2.63	Blue	.....	
5.00	+3.03	Blue	+1.26	Blue
	B_2 horizon		C_2 horizon	
0	−1.29		−1.44	
0.25	−0.84	Colorless	−0.30	Colorless
0.50	.....		+0.87	Very light blue
0.75	−0.34	Colorless	+1.21	Light blue
1.00	+0.50	Nearly colorless	+2.33	Blue
1.25	+1.21	Very light blue	+3.03	Blue
1.75	+1.26	Light blue	+3.37	Blue
2.25	+2.02	Blue	+3.79	Blue
3.25	+2.42	Blue	+4.04	Blue
5.00	+3.03	Blue	+4.67	Blue

sult. At the same time, as the acid residues in the colloid complexes of these soils decrease in strength—but, as pointed out, not necessarily in amount—with increasing depth, the basic residues increase, not only in strength but also in amount, at least to the B horizon. We would expect, therefore, to

find a low adsorption of acid dyes in the A horizon and a high one in B. A decline in C is possible because of lower amounts of colloids present. From a theoretical standpoint we should not expect to find a complete adsorption of the acid dye on the electronegative side of the isoelectric point but, on the contrary, possibly on the electropositive side. It was also proved experimentally with the soils used for the cataphoretic experiments with night blue that increasing concentrations of an acid dye—alizarine red R—caused an increasing electronegative velocity of the particles. If a suitable concentration of HCl was added, concentrations of the dye could be found which made the complex isoelectric. It is to be deplored that the dye used in the experiments has so weak a color in acid solutions as to make it impossible to determine colorimetrically if and when the adsorption is complete.

From a scientific standpoint it would naturally be best to determine the highest amount of dye completely adsorbed from a solution. This would give values most characteristic for each soil. But because of the difficulties mentioned with the acid dye, this method was not used except in the experiments just reported. Instead a very simple colorimetric method was applied which, though for apparent reasons not giving absolutely comparable results, makes comparative studies of different soil types very easy and rapid. It was used in the following way. A soil sample was repeatedly shaken for a day with a dye solution strong enough to leave some of the dye unadsorbed. The test tubes were left undisturbed overnight; a part of the clear solutions was taken out with a pipette and diluted to a convenient volume; and the amount of dye was colorimetrically determined in a comparator against standard solutions of the dye. From the amount thus determined and the original volume and concentration the amount adsorbed was calculated. The dyes used were night blue, methylene blue (both basic), and alizarine red R (acid). Night blue was found unsuitable for the purpose because of changes of color at different reactions. Methylene blue, however, was found to have a constant color within the pH range of the soils investigated and far beyond on both sides. Since the strength of color is proportionate to the dilution within reasonable limits, the dye is ideal from the viewpoint of colorimetric determinations. Alizarine red R is red in alkaline solutions and yellow in acid. Its point of color change lies within the pH range of the soils, and therefore the samples taken out for estimation must be treated with alkali or acid to get the full color on either side. The alkali color was found suitable for colorimetric work, since it was proportionate to the dilution and fairly strong. The yellow acid color cannot be used, since it is impossible to determine small differences in dilute solutions.

In order to obtain information about the dye adsorption of colloids with different composition, experiments were made with artificial alumino-silicates.[2]

[2] These were prepared by Dr. J. S. Csiky, who at the same time was making other investigations with them at the New Jersey Agricultural Experiment Station. The author wishes to thank Dr. Csiky for his friendliness in supplying samples of this valuable material.

The alumino-silicates were completely electrodialyzed, and the composition, here quoted as the SiO_2/Al_2O_3 ratio, was determined by Dr. Csiky. The experiments were made in the following way. Samples of 0.2 gm. of each silicate were shaken in test tubes with 10 cc. of dye solution of different concentrations in the way previously described; the unadsorbed dye was estimated colorimetrically and the adsorbed amounts were calculated. The results are

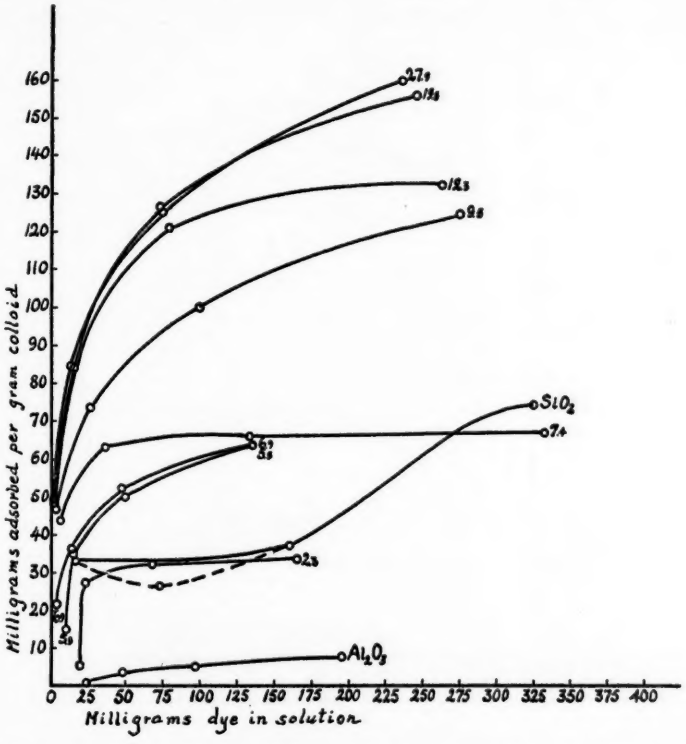

FIG. 13. ADSORPTION OF METHYLENE BLUE FROM SOLUTIONS OF DIFFERENT STRENGTHS BY ARTIFICIAL ALUMINO-SILICATES

The figures at the ends of the curves are the silica/alumina ratios

seen in figures 13, 14 and 15. Objection to figures 13 and 14 may be raised on the ground that three or four points are not enough to permit the drawing of a curve. These curves, however, are not intended to be used for any exact determinations of the process of adsorption but only to show the influence of the composition on the adsorption.

Let us first look at the adsorption curves for methylene blue (fig. 13). It is seen that all the curves (except the SiO_2 curve) are of the same form, namely,

that of the familiar "adsorption" curves: in low concentrations the dye is proportionally far more extensively adsorbed than in higher concentrations. The amount adsorbed seems to reach asymptotically a certain maximum independent of a further increase in the concentration of the supernatant liquid. This maximum is not reached, at the concentrations used, in the case of alumino-silicates with a very high SiO_2/Al_2O_3 ratio. The adsorption is higher the wider this ratio, being lowest in the pure aluminum hydroxide, in accordance with the theory the greater the acid residue in the colloid the

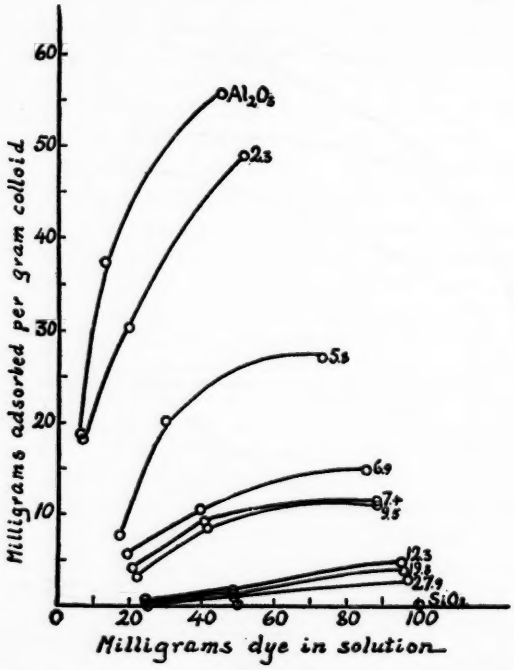

FIG. 14. ADSORPTION OF ALIZARINE RED R FROM SOLUTIONS OF DIFFERENT STRENGTHS BY ARTIFICIAL ALUMINO-SILICATES

The figures at the ends of the curves are the silica/alumina ratios

higher its adsorption for the methylene blue cation. The pure SiO_2 is an exception: the adsorption is here even lower than that for many of the silicates with a rather narrow SiO_2/Al_2O_3 ratio. This might depend on the mode of preparation: the silica was not prepared like the silicates (by precipitation from sodium silicate with HCl and subsequent electrodialysis) but was a commercial product electrodialyzed for purification. Here we must take into consideration aging of the colloid and various differences in the state of aggregation which might affect the adsorbing capacity. But it is not impossible that the

dye adsorption has a maximum at some wide SiO_2/Al_2O_3 ratio, just as the base exchange, according to Csiky's results, has a maximum at a certain

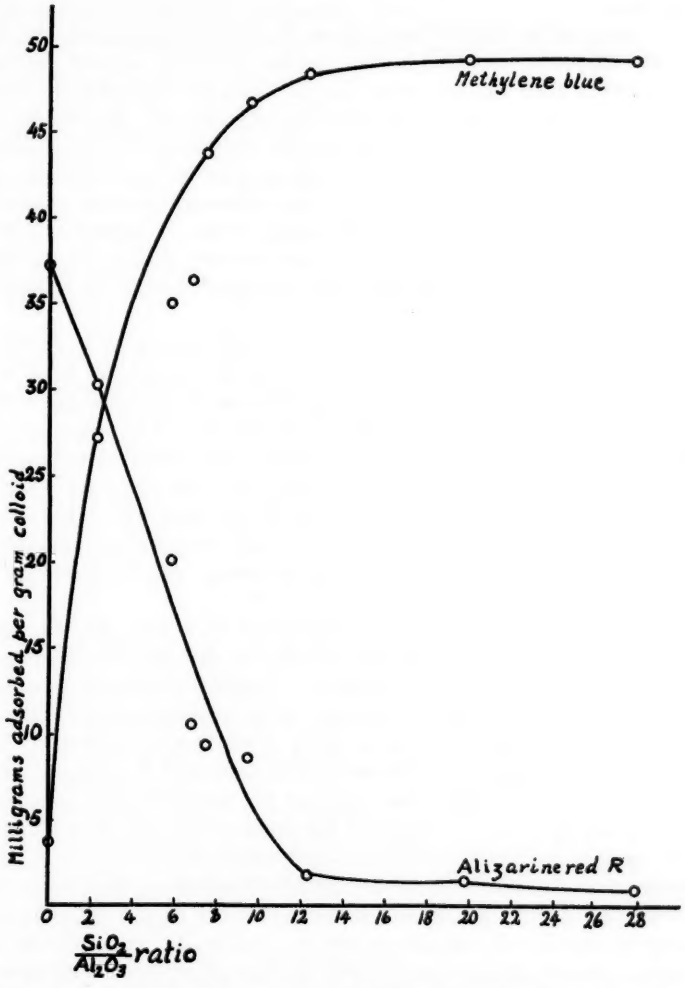

FIG. 15. THE RELATIONSHIP BETWEEN THE COMPOSITION OF ALUMINO-SILICATES AND THEIR ADSORPTION OF METHYLENE BLUE AND ALIZARINE RED R
50 mgm. of the dye added in each case

composition of the silicate and decreases on both sides of this value. If actually existent, the maximum in the case of the dye adsorption must lie

above the ratio 27.9, i.e., at a much wider ratio than the maximum of base exchange. The reason for this difference might be sought in the low degree of dissociation and hence in the slight hydrolysis of the methylene blue compounds.

The adsorption of alizarine red R gives the same type of curves (fig. 14), the only difference being that in this case the adsorbing capacity decreases with increasing silica/alumina ratio: the more basic the residues in the colloid complex, the higher the adsorption of anions; the more acid the residues, the lower the adsorption of such ions. In this case the pure silica is no exception: it shows no adsorption of the acid dye, just as would be expected with a colloid of pure acidoid character with no perceptible ampholytoid properties. The pure alumina also fits well in the series: it has the highest adsorbing capacity, as would be expected from its ampholytoid nature, for the basic residues should decrease in strength when acidoids like silica are introduced into the complex.

After the work on dye adsorption was completed a paper by F. Hardy on alizarine adsorption of soils, minerals, and artificial alumina and ferric oxide came to hand (1). Hardy does not work with exactly the same dye as here used but with sodium alizarine sulfonate (alizarine S), but its properties seem to be closely related to those of alizarine red R. His method of estimation is also colorimetric, but the dye adsorbed is extracted with a solution of sodium oxalate containing an excess of oxalic acid, the pH being 3.8. This necessitates corrections for the iron dissolved. A still more serious complication would probably arise in the case of soils containing appreciable amounts of organic matter.

Some objections to Hardy's interpretation of his results may be made. The calculations are founded on the assumption that the soils contain the hydrous sesquioxides in a "free" condition. Even if this is the case in lateritic soils formed at reactions within the range of the isoelectric points of the free sesquioxides themselves, there is no proof of the general existence of free sesquioxides in the soil. A multitude of facts concerning the chemical nature of soil colloids tend to show that they are not single chemical compounds occurring side by side, but complexes composed of the acidoids and ampholytoids present, the relative amounts of the components and the type of linking between them depending on the soil forming conditions. The assumption that the "total" adsorption was determined cannot be correct because the adsorption depends on the circumstances. Just as, for instance, the base exchange capacity depends on the pH, the dye adsorption, which is to be considered as an ion exchange, depends on the same quality and thus on the concentration of the solution. This fact is also demonstrated experimentally with the dyes used in the experiments here reported.

These critical remarks on Hardy's work are made only in order to get a truer interpretation of the results. The idea of using the adsorption of dyes as a means of investigating the genesis of soils is very promising, and there-

fore Hardy's work is of great importance. One thing which should be further investigated is the significance of the alizarine adsorption by ignited alumina as against the nonadsorption by some of its natural hydrated compounds.

Let us now return to our soil profiles. Two 2-gm. samples (calculated as oven-dry material) of each soil were repeatedly shaken for a day in test tubes

TABLE 8

Adsorption of methylene blue and alizarine red R from 0.1 per cent solutions by samples from podzols and brown forest soils

Milligrams per gram soil

PROFILE NUMBER	SOIL TYPE	HORIZON	AMOUNTS ADSORBED		PROFILE NUMBER	SOIL TYPE	HORIZON	AMOUNTS ADSORBED	
			Methylene blue	Alizarine red R				Methylene blue	Alizarine red R
1	Brown forest soil (typical)	A	10.85*	2.73	2	Podzol	A_2	3.56	0.00
		B_1	4.55	1.00			B_1	1.74	0.69
		B_2	3.93	0.73			B_2	1.05	1.08
		C_1	1.14	0.66			C_1	0.74	1.00
		C_2	1.59	0.54			C_2	0.43	0.00
3	Brown forest soil (aclimatic)	A	62.18†	4.75	4	Iron podzol	A_2	2.76	0.00
		B_1	4.50	0.00			B_1	1.67	0.60
		B_2	2.45	0.20			B_2	1.46	0.05
		B_3	2.89	0.29			C	0.95	0.00
		C	1.88	0.05					
					6	Iron podzol	A_0	40.95‡	4.80
5	Iron podzol	A_2	2.18	0.00			A_2	3.27	0.00
		B_1	2.00	0.75			B	1.67	3.26
		B_2	0.88	0.55			C	0.40	0.20
		C_1	0.67	0.24					
		C_2	0.77	0.39					
		C_3	0.74	0.20					
7	Iron humus podzol	A_2	3.21	0.00					
		B_1	3.37	1.30					
		B_2	4.36	0.84					
		C	2.78	0.00					

* From 17 mgm. added.
† From 64 mgm. added.
‡ From 43 mgm. added.

with 10 cc. of an aqueous solution containing 1 mgm. per cubic centimeter of methylene blue or alizarine red R. The next day 5 cc. of the clear solutions was pipetted off from each test tube; the amount of dye present was colorimetrically estimated; and, from the results, the amounts adsorbed were calculated in milligrams per gram of soil (table 8). In some cases where the

amount added was totally adsorbed new amounts of more concentrated dye solution were added until the solution remained colored.

The podzol profiles show a high adsorption of methylene blue in the A_2 horizon and a gradual decrease through B and C. Sometimes the adsorption in A_2 is twice as high as in B, though the amount of colloids is generally low in A_2. Thus the qualitative properties of the colloids are clearly expressed. The lack of agreement with, for instance, the combining capacities reported in table 6 (5) is accounted for by the fact that the methylene blue adsorption took place at a *relatively* lower pH, i.e., nearer to the isoelectric point, in the case of the B and C samples. The more strongly acidoid A_2 shows, therefore, a relatively greater adsorption of the dye than that corresponding to the combining capacities at pH 7. Only in the case of the iron humus podzol do we find a higher adsorption in B than in A_2. As has been stated, however, this type of podzol is characterized by a very high content of colloids in the B horizon; furthermore, this horizon is rich in organic matter. These things account for the difference. The adsorption of alizarine red gives, as predicted, even more distinct proofs of the qualitative properties of the different soil horizons and their colloids. Being an acid dye it is not adsorbed at all in the A_2 horizon just as it is not adsorbed by the pure silica. In the B horizon with its comparatively high content of ampholytoid material there is always a very marked adsorption. In the deeper parts of the profile there is a decrease, as might be expected, because of the decline in the amounts of colloids present. Sometimes no adsorption was found in C, which would perhaps seem remarkable. It should be remembered, however, that the soils investigated are "young" soils developed during the few thousand years since the last glaciation. The parent material, a moraine, consists chiefly of mechanically disintegrated rocks. These rocks, porphyries, sandstones, and granites, are composed of minerals which perhaps do not adsorb alizarine red R, just as they, according to Hardy, do not adsorb alizarine S (1, p. 155). Thus the method employed, in cases like those here presented, would possibly give a fairly accurate determination of the depth to which the soil forming processes have proceeded. In the A_0 layer the adsorption of methylene blue is very high, as indicated by the results in profile 6. This might also be expected, because of the high content of acid humus. It is noteworthy, however, that the alizarine adsorption also is high in A_0. This must certainly depend on basoid or ampholytoid organic compounds in the soil colloid complex, such as the proteins, since the mineral compounds, judged from the properties of the A_2 horizon, hardly can adsorb this dye in appreciable amounts.

In the case of the brown forest soil we find the same type of methylene blue adsorption as in the podzols, i.e., the adsorption is very high in A and decreases gradually through B and C. This should indicate that the acidoid character of the soil colloid complex decreases with increasing depth. But it must be remembered that the amount of colloids, especially of the organic matter, is higher in the upper parts of the profile, and thus the results are not conclusive.

The alizarine adsorption varies in exactly the same way: it is high in A and then decreases. This does not necessarily mean, because of the difference in the amounts of colloid present, that the basic residues in the colloids decrease with increasing depth. But the results show a clear difference between the podzols and the brown forest soils. In the case of the latter soil type ampholytoid compounds of the colloid complex remain in appreciable amounts throughout the entire A horizon, as well as in B, as against the total absence of basic residues strong enough to adsorb alizarine in the A_2 horizon of podzols. The conclusion must be that the type of weathering leading to the formation of a brown forest soil is of far less acid character than that leading to a podzol.

The case of the aclimatic brown forest soil is interesting. At first we note the very high adsorption of methylene blue in A, even higher than the one recorded for A_0 of the iron podzol 6, though the percentage of organic matter as well as the acidity is lower. But nearly all organic matter is probably colloidal in the case of the brown forest soil mull as against the coarse nearly undecomposed organic residues of the podzol duff, and this certainly accounts for the difference. The adsorption of methylene blue then decreases through B and C in about the way described for the other soils. The alizarine adsorption is most interesting. It is high in A, absent in the upper B, increasing in the deeper parts of B, and very low in C. This means that the ampholytoids present in B_1 have basic residues so weak as not to be able to adsorb any alizarine anions, because of acidoids present, though the amounts of ampholytoids are rather high [compare the high amounts of sesquioxides found with the acid-oxalate method (4, p. 149)]. The results show that the aclimatic brown forest soil, in its properties, stands between the typical brown forest soil and the podzols. The type of weathering is less acid than that of the podzols, allowing sesquioxides to remain as an important part of the colloid complex even in the upper parts of the profile. At the same time, however, the acidoids are strong enough to "neutralize" the basoid groups of the ampholytoids to a far greater extent than in the typical brown forest soils.

The results of experiments with dye adsorption may be summarized as follows. Basic dyes, such as methylene blue, are strongly adsorbed by soil colloids rich in acid residues. Acid dyes, such as alizarine red R, are in the same manner adsorbed by soil colloids rich in basic residues. The qualitative and approximately quantitative properties of the colloids thus established aid in the study of the soil profiles. They also permit a comparison between different soil types. The theory of isoelectric weathering is confirmed by the results obtained, and it could be shown that the brown forest soils are the result of a less acid weathering than are the podzols. It could even be demonstrated that an aclimatic brown forest soil in its colloidal properties takes a middle position between podzols and typical brown forest soils. The alizarine adsorption may also perhaps under certain conditions be used as a means of determining how deep the soil forming processes are apparent in a soil profile. Whether the dyes here used are the most suitable may be left to further inves-

tigations. Hardy has proposed the use of haematoxylin (1, p. 164). Many other dyes, both basic and acid, should be tested in order to determine the best method.

SUMMARY

The podzol and brown forest soil profiles dealt with in the first and second parts of this paper are further investigated as to their power of dye adsorption.

Experiments with artificial alumino-silicates show that the dye adsorption is comparable to the ion adsorption of colloids.

The adsorption of acid and basic dyes is a promising method for a rapid and conclusive investigation of the colloidal properties of a soil. For a tentative investigation the colorimetric method described in this paper seems to give enough information. Scientifically more conclusive results will be obtained by determining the adsorption of the dye at a definite pH value which should lie above and below the isoelectric point for the basic and acid dye respectively.

Methods such as those used in the three parts of this paper will permit a rapid and conclusive comparative study of the soil forming processes in different soil regions. Acid-oxalate determinations of the reactive part of the colloids or the easy methods of investigating the amphoteric properties of the soil colloids—especially determinations of the ultimate pH, the pH of exchange neutrality, the combining capacity at different pH values, and the adsorption of acid and basic dyes—are very valuable in comparative studies where many analyses are necessary. For a thorough knowledge of the soils total chemical analyses are necessary; for many purposes, however, they may be confined to a few type specimens of the soils and the comparative study made with the easy and rapid methods here applied.

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BOOK REVIEW

Humus. Origin, Chemical Composition, and Importance in Nature. By SELMAN A. WAKSMAN, professor of soil microbiology, Rutgers University, and microbiologist, New Jersey Agricultural Experiment Station. The Williams & Wilkins Co., Baltimore, 1936. Pp. xi + 494, figs. 45, tables 63. Price $6.50.

One who has followed the numerous reports of the author's researches on the microbial transformation of organic materials is familiar with the subjects receiving particular emphasis in this monograph, for it is about the subject matter of these reports that the treatise is developed and considerably extended. It is far more than a recapitulation of this material, involving a thorough and careful consideration of the extensive literature on the properties and importance of the organic formations found in nature. The author's investigations of the last fifteen years have yielded much new information which has revised the conception of the nature of soil organic matter and of the processes leading to its formation. His critical and keen interpretation of the facts, his originality of approach, and his broad appreciation of the many aspects of the subject have resulted in the creation of logical order from the confused and seemingly contradictory evidence in the scientific literature. In any attempt to coördinate such conflicting views as pervade the subject it is almost inevitable that there will be divergence of opinion. It is with temerity that most persons would assume the task; particular commendation is therefore due the author for having so effectively surmouted the difficulties.

According to the author: "This book is an attempt to tell the story of humus, its origin from plant and animal residues, its chemical composition, its physical properties, its importance in nature, especially in soil processes and in plant growth, and finally its decomposition.... Humus is a complex aggregate of brown to dark colored amorphous substances, which have originated during the decomposition of plant and animal residues by microörganisms, under aerobic and anaerobic conditions, usually in soils, composts, peat bogs, and water basins.... The chemical composition of humus is determined by the nature of the residues from which it is formed, by the conditions of its decomposition, and by the extent to which it is decomposed. Chemically, humus consists of numerous organic complexes, the major group of which consists of lignins and lignin derivatives and of proteins; a minor group contains carbohydrates, fats, organic acids, alcohols, and other carbon compounds."

The use of such terms as "humins," "ulmins," "crenic acid," "apocrenic acid," and others as they are applied to preparations is considered by the

author to be unwarranted. He prefers to characterize humus by the relative proportions of the various chemical substances such as cellulose, hemicelluloses, lignin, proteins, etc., which it contains. More information concerning lignin in particular, its composition, characteristic properties, and decomposition, is still needed to complete an understanding of the behavior of the soil organic matter.

Although there is considerable emphasis upon the chemical and physical properties of humus as a whole and of its specific constituents, principal attention is directed to the activities of microörganisms in determining the nature of the residues and products of decomposition which characterize the humus. Among the organic substances considered, other than soil humus, are plant residues, animal manures, peat, coal, and organic matter in waters. The practical importance of these materials is indicated, but chief attention is focussed upon the fundamental principles which should be the basis of agricultural practices.

A list of chapter titles inadequately suggests the variety of subjects considered: The rôle of humus in the organic cycle in nature; Nature and characteristics of humus; The rôle of humus in plant nutrition; The changing conceptions concerning the chemical nature of "humus" and "humic acids"; "Humification" of organic matter in soils and in composts, and methods of "humus" determination; Origin of humus; Isolation of definite organic chemical compounds from humus; Chemical nature of humus as a whole; Humus formation in composts, animal manures, and green manures; Humus in forest and heath soils; Humus in mineral soils (field, grassland, garden, and orchard); Humus in peat and in coal; Organic matter formations in water systems; Physical and physicochemical properties of humus; Decomposition of humus in nature; Presence in humus of specific substances which have an injurious or a beneficial effect upon growth of plants, animals and microörganisms; Utilization of various forms of humus for agricultural and industrial purposes; Soil humus and the science of pedology; Humus as an organic system; Appendix —Methods of analysis of humus and of certain humus constituents.

There are 1311 items in the bibliography, including many more than this number of individual references. There are both author and subject indexes.

This volume should prove useful to all who are concerned with the most profitable use and conservation of the natural resources of organic materials, particularly to students of soils and plants.

ROBERT L. STARKEY.